

EPA/DOE

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# MINE WASTE TECHNOLOGY PROGRAM

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Technology Testing for Tomorrow's Solutions



## 1999 ANNUAL REPORT

EPA DOE Montana Tech Implemented by MSE, Inc.

# CONTENTS

	Page
Vision Statement for the Butte Mine Waste Technology Program . . . . .	1
Program Manager's Executive Summary . . . . .	3
Introduction . . . . .	5
Program Overview . . . . .	7
Organizational Structure . . . . .	9
Activities . . . . .	11
Descriptions, Accomplishments, and Future Direction . . . . .	11
Activity I Overview—Issues Identification . . . . .	11
Activity II Overview—Quality Assurance . . . . .	11
Activity III Overview—Field Demonstrations . . . . .	12
Project 3    Sulfate-Reducing Bacteria Demonstration . . . . .	12
Project 8    Underground Mine Source Control . . . . .	14
Project 10   Surface Waste Piles—Source Control . . . . .	15
Project 11   Cyanide Heap Biological Detoxification Demonstration . . . . .	16
Project 12   Sulfate-Reducing Bacteria Reactive Wall Demonstration . . . . .	20
Project 12A  Calliope Mine Internet Monitoring System . . . . .	23
Project 13   Hydrostatic Bulkhead with Sulfate-Reducing Bacteria . . . . .	25
Project 14   Biological Cover Demonstration . . . . .	26
Project 15   Tailings Source Control . . . . .	27
Project 16   Integrated Passive Biological Treatment Process Demonstration . . . . .	28
Project 17   Lead Abatement Demonstration . . . . .	28
Project 18   Gas-Fed Sulfate-Reducing Bacteria Berkeley Pit Water Treatment . . . . .	31
Project 19   Site In Situ Mercury Stabilization Technologies . . . . .	32
Project 20   Selenium Removal/Treatment Alternatives . . . . .	33
Project 21   Integrated Process for Treatment of Berkeley Pit Water . . . . .	35
Project 23   Revegetation of Mining Waste Using Organic Soil Amendments and Evaluate the Potential for Creating Attractive Nuisances for Wildlife . . . . .	36
Activity IV Overview . . . . .	37
Project 8    Pit Lake System—Characterization and Remediation for the Berkeley Pit . . . . .	37
Project 9    Pit Lake System—Deep Water Sediment/Pore Water Characterization and Interactions . . . . .	37
Project 10   Pit Lake System—Biological Survey of Berkeley Pit Water . . . . .	38
Project 11   Pit Lake System Characterization and Remediation for Berkeley Pit—Phase II . . . . .	39

Activity V Overview—Technology Transfer . . . . .	40
Activity VI Overview—Training and Education . . . . .	41
Financial Summary . . . . .	43
Completed Activities . . . . .	45
Activity III	
Project 1 Remote Mine Site Demonstration . . . . .	45
Project 2 Clay-Based Grouting Demonstration . . . . .	46
Project 4 Nitrate Removal Demonstration . . . . .	46
Project 5 Biocyanide Demonstration . . . . .	47
Project 6 Pollutant Magnet . . . . .	48
Project 7 Arsenic Oxidation . . . . .	49
Project 9 Arsenic Removal . . . . .	49
Activity IV	
Project 1 Berkeley Pit Water Treatment . . . . .	50
Project 2 Sludge Stabilization . . . . .	51
Project 3 Photoassisted Electron Transfer Reactions Research . . . . .	52
Project 3A Photoassisted Electron Transfer Reactions for Metal-Complexed Cyanide . . . . .	53
Project 3B Photoassisted Electron Transfer Reactions for Berkeley Pit Water . . . . .	54
Project 4 Metal Ion Removal from Acid Mine Wastewaters by Neutral Chelating Polymers . . . . .	55
Project 5 Removal of Arsenic as Storable Stable Precipitates . . . . .	56
Project 7 Berkeley Pit Innovative Technologies Project . . . . .	57
Key Contacts . . . . .	59

# VISION STATEMENT FOR THE BUTTE MINE WASTE TECHNOLOGY PROGRAM

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## THE PROBLEM

Mining activities in the United States (not counting coal) produce between 1 and 2 billion tons of mine waste annually. These activities include extraction and beneficiation of metallic ores, phosphate, uranium, and oil shale. Over 130,000 of these noncoal mines, concentrated largely in nine western states, are responsible for polluting over 3,400 miles of streams and over 440,000 acres of land. About seventy of these sites are on the National Priority List for Superfund remediation. In the 1985 Report to Congress on the subject, the total noncoal mine waste volume was estimated at 50 billion tons, with 33% being tailings, 17% dump/heap leach wastes and mine water, and 50% surface and underground wastes. Since many of the mines involve sulfide minerals, the production of acid mine drainage (AMD) is a common problem from these abandoned mine sites. The cold temperatures in the higher elevations and heavy snows frequently prevent winter site access. The combination of acidity, heavy metals, and sediment have severe detrimental environmental impacts on the delicate ecosystems in the West.

## THE PHILOSOPHY/VISION

End-of-pipe treatment technologies, while essential for short-term control of environmental impact from mining operations, are a stop-gap approach for total remediation. Efforts need to be made on improving the end-of-pipe technologies to reduce trace elements to low levels for applications in ultra-sensitive watersheds and for reliable operation in unattended, no power situations. The concept of pollution prevention, emphasizing at-source control and resource recovery, is the approach of choice for the long-term solution. Our objective in the Butte Mine Waste Technology Program is not to assess the

environmental impacts of the mining activities, but it is to develop and prove technologies that provide satisfactory short- and long-term solutions to the remedial problems facing abandoned mines and the ongoing compliance problems associated with active mines, not only in Montana but throughout the United States.

## THE APPROACH

There are priority areas for research, in the following order of importance:

### **Source Controls, Including In Situ Treatments and Predictive Techniques**

It is far more effective to attack the problem at its source than to attempt to deal with diverse and dispersed wastes, laden with wide varieties of metal contaminants. At-source control technologies, such as sulfate-reducing bacteria; biocyanide oxidation for heap leach piles; transport control/pathway interruption techniques, including infiltration controls, sealing, grouting, and plugging by ultramicrobiological systems; and AMD production prediction techniques should strive toward providing a permanent solution, which of course is the most important goal of the program.

### **Treatment Technologies**

Improvements in short-term end-of-pipe treatment options are essential for providing immediate alleviation of some of the severe environmental problems associated with mining, and particularly with abandoned ore mines. Because immediate solutions may be required, this area of research is extremely important to effective environmental protection.

### **Resource Recovery**

In the spirit of pollution prevention, much of the mining wastes, both AMD (e.g., *over 25 billion*

*gallons* of Berkeley Pit water) and the billions of tons of mining/beneficiation wastes, represent a potential resource as they contain significant quantities of heavy metals. While remediating these wastes, it may be feasible to incorporate resource recovery options to help offset remedial costs.

## THE PARTNERSHIPS

In these days of ever-tightening budgets, it is important that we leverage our limited funding with other agencies and with private industry. We are aggressively working to integrate the Butte program with the U.S. Department of Energy Resource Recovery Project to leverage both budgets. The Bureau of Land Management and Forest Service participate by providing sites for demonstrations of the technologies. It is important where these technologies have application to active mining operations to achieve cost-sharing partnerships with the mining industry to test the technologies at their sites. Within the U.S. Environmental Protection Agency, the Butte program is coordinated and teamed, where appropriate, with the Superfund Innovative Technology Evaluation (SITE) program to leverage the funding and maximize the effectiveness of both programs. Several joint projects are underway, and more are planned.

A considerable resource and willing partner is the University system (such as Montana Tech of the University of Montana, University of Montana–Missoula, Montana State University–Bozeman, and the Center for Biofilm Engineering), which can conduct the more basic type of research essential to kinetics characterization and bench-scale test more experimental, less developed concepts at minimal cost to the program, while at the same time providing environmental education that will be useful to the region and to the Nation. The Butte Mine Waste Technology Program supports cooperative projects between the educational system and the mining industry, where teams of students conduct research of mine site-specific problems, often with monetary support from the industry. The results are made available to the industry as a whole and to the academic community.

## THE SCIENCE

The research program is peer-reviewed semiannually by the Technical Integration Committee (TIC), who technically reviews all ongoing and proposed projects. The TIC is composed of technical experts from the cooperating agencies, academia, environmental stakeholders, and industry and their consultants.

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# PROGRAM MANAGER'S EXECUTIVE SUMMARY

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The Mine Waste Technology Program (MWTP) Annual Report for fiscal year 1999 summarizes the results and accomplishments for the various activities within the Program. The MWTP has met its goals by providing assistance to the public and forming cooperative teams drawn from Government, industry, and private citizens. The funds expended have returned tangible results, providing tools for those faced with mine waste remediation challenges.

After 8 years, everyone involved with MWTP can look with pride to the Program's success. Technology development has proceeded successfully through the efforts of MSE Technology Applications Inc. (MSE) and its prime subcontractor Montana Tech.

MSE has developed twenty-one field-scale demonstrations, several of which are attracting attention from the stakeholders involved in the cleanup of mine wastes.

Montana Tech has developed eleven bench-scale projects, five of which are ongoing during 1999.

Numerous activities are associated with the development of a field-scale demonstration. Among these activities are acquiring federal and state permits, securing liability limiting access agreements, developing and adhering to health and safety operation plans, and complying with the National Environmental Policy Act and other federal and state environmental oversight statutes.

The Program has received substantial support from state and federal agencies, the mining industry, environmental organizations, and numerous associations interested in mining and development of natural resources at state, regional, and national levels.

Montana Tech continued the post-graduate degree program with a mine waste emphasis in which sixty students have enrolled. The quality of short courses offered by Montana Tech is becoming highly recognized among the mine waste remediation community.

The MWTP recognizes its major accomplishments and looks forward to providing new and innovative technologies; meeting the challenges of mine waste remediation; and providing low cost, permanent solutions to the nation's mineral waste problems.

Creighton Barry  
MSE MWTP Program Manager



# INTRODUCTION

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Mining waste generated by active and inactive mining production facilities and its impact on human health and the environment are a growing problem for Government entities, private industry, and the general public. The nation's reported volume of mine waste is immense. Presently, there are 68 sites on the U.S. Environmental Protection Agency's (EPA) National Priorities List.

Environmental impacts associated with inactive and abandoned mines are common to mining districts around the country, as shown in Table 1.

Total estimated remediation costs for these states range from \$4 to \$45 billion.

Health effects from the predominate contaminants in mine waste range from mild irritants to proven human carcinogens, such as cadmium and arsenic. The large volume of mine wastes and consequential adverse environmental and human health effects indicates an urgency for cleanup of abandoned, inactive, and active mining facilities. The environmental future of the United States depends in part on the ability to deal effectively with mine waste problems of the past and present, and, more importantly, to prevent mine waste problems in the future.

According to a 1985 report to Congress, mining and related activities generate anywhere from 1 to 2

billion tons of waste each year with a current total waste volume of 50 billion tons. Of this total volume, approximately 85% is attributed to copper, iron ore, uranium, and phosphate mining and related activities. Approximately one-half of the waste generated is mining waste and one-third is tailings, with the balance consisting of dump/heap leaching wastes and mine water.

The fiscal year (FY) 1991 Congressional Appropriation allocated \$3.5 million to establish a pilot program in Butte, Montana, for evaluating and testing mine waste treatment technologies. The Mine Waste Technology Program (MWTP) received additional appropriations of \$3.5 million in FY91, \$3.3 million in FY94, \$5.9 million in FY95, \$2.5 million in FY96, \$7.5 million in FY97, and \$6.0 million in FY98 and FY99.

The projects undertaken by this Program focus on developing and demonstrating innovative technologies at both the bench-and pilot-scale that treat wastes to reduce their volume, mobility, or toxicity. To convey the results of these demonstrations to the user community, the mining industry, and regulatory agencies, MWTP includes provisions for extensive technology transfer and educational activities. This report summarizes the progress MWTP made in FY99.



**Table 1. Number and types of sites and abandoned mine lands in Western Region.**

State	Estimated Number of Sites or Land Areas	Classification and Estimated Number
Alaska	10,910 sites	mine dumps - 1,000 acres disturbed land - 27,680 acres mine openings - 500 hazardous structures - 300
Arizona	95,000 sites	polluted water - 2,002 acres mine dumps - 40,000 acres disturbed land - 96,652 acres mine openings - 80,000
California	11,500 sites	polluted water - 369,920 acres mine dumps - 171 acres mine openings - 1,685
Colorado	20,229 sites covering 26,584 acres	polluted water 830,720 acres mine dumps - 11,800 acres disturbed land - 13,486 acres mine openings - 20,229 hazardous structures - 1,125
Idaho	8,500 sites covering 18,465 acres	polluted water - 84,480 acres mine dumps - 3,048 acres disturbed land - 24,495 acres mine openings - 2,979 hazardous structures - 1,926
Michigan	400-500 sites	Accurate information not available.
Montana	19,751 sites covering 11,256 acres	polluted water - 715,520 acres mine dumps - 14,038 acres disturbed land - 20,862 acres mine openings - 4,668 hazardous structures - 1,747
Nevada	400,000 sites	Accurate information not available.
New Mexico	7,222 sites covering 13,585 acres	polluted water - 44,160 acres mine dumps - 6,335 acres disturbed land - 25,230 acres mine openings - 13,666 hazardous structures - 658
Oregon	3,750 sites	polluted water - 140,800 acres mine dumps - 180 acres disturbed land - 61,000 acres mine openings - 3,750 hazardous structures - 695
South Dakota	4,775 acres	Accurate information not available.
Texas	17,300 acres	Accurate information not available.
Utah	14,364 sites covering 12,780 acres	polluted water - 53,120 acres mine dumps - 2,369 acres disturbed land - 18,873 acres mine openings - 14,364 hazardous structures - 224
Wisconsin	200 acres	Accurate information not available.
Wyoming	5,000 acres	Accurate information not available.
Information was collected from the following sources and is only an estimate of the AMD problem in the West.		
<div> -Bureau of Land Management  -Bureau of Mines  -Mineral Policy Center  -National Park Service  -U.S. Department of Agriculture </div> <div> -U.S. Department of the Interior  -U.S. Forest Service  -U.S. Geological Survey  -U.S. General Accounting Office  -Western Governor's Association Mine Waste Task Force Study </div>		

# PROGRAM OVERVIEW

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## FISCAL YEAR 1999 PROGRAM

This MWTP annual report covers the period from October 1, 1998, through September 30, 1999. This section of the report explains the organization and operation of MWTP.

## MISSION

The mission of MWTP is to provide engineering solutions to national environmental issues resulting from the past practices of mining and smelting metallic ores. In accomplishing this mission, MWTP develops and conducts a program that emphasizes treatment technology development, testing and evaluation at bench- and pilot-scale, and an education program that emphasizes training and technology transfer. Evaluation of the treatment technologies focuses on reducing the mobility, toxicity, and volume of waste; implementability; short- and long-term effectiveness; protection of human health and the environment; community acceptance; and cost reduction.

The statement of work provided in the Interagency Agreement between EPA and the U.S. Department of Energy (DOE) identifies six activities to be completed by MWTP. The following descriptions identify the key features of each and the organization performing the activity.

## ACTIVITY I: ISSUES IDENTIFICATION

Montana Tech of the University of Montana (Montana Tech) is documenting mine waste technical issues and innovative treatment technologies. These issues and technologies are then screened and prioritized in volumes related to a specific mine waste problem. Technical issues of primary interest are Mobile Toxic Constituents—Water/Acid Generation; Mobile Toxic Constituents—Air, Cyanide, Nitrate, Arsenic,

Pyrite, Selenium, Thallium; and Pit Lakes. Wasteforms reviewed related to these issues include point- and nonpoint-source acid drainage, abandoned mine acid drainage, stream-side tailings, impounded tailings, priority soils, and heap leach-cyanide/acid tailings.

## ACTIVITY II: GENERIC QUALITY ASSURANCE PROJECT PLAN

Montana Tech has prepared a generic quality assurance project plan that provides specific instructions on how data will be gathered, analyzed, and reported for all activities of MWTP. Features of both EPA and DOE quality requirements are incorporated into this plan. Project-specific quality assurance project plans are developed by MSE Technology Applications, Inc. (MSE). MSE provides oversight for all quality assurance activities.

## ACTIVITY III: PILOT-SCALE DEMONSTRATIONS

MSE began six field-scale demonstrations during FY99. The demonstration topics were chosen after a thorough investigation of the associated technical issue was performed, the specific waste form to be tested was identified, two levels of peer review were conducted, and sound engineering and cost determination of the demonstration were formulated.

## ACTIVITY IV: BENCH-SCALE EXPERIMENTS

Montana Tech successfully completed three bench-scale projects during FY99: 1) Pit Lake System—Characterization and Remediation for the Berkeley Pit; 2) Pit Lake System—Deep Water Sediment/Pore Water Characterization and Interactions; and 3) Pit Lake System—Biological

Survey of Berkeley Pit Water. In addition, Project 11, Pit Lake System Characterization and Remediation for Berkeley Pit—Phase II, was begun, which assesses the effect on organic carbon, wall rock/water interactions, bacteria for natural remediation, and the effect of redepositing neutral tailings into the Berkeley Pit.

## **ACTIVITY V: TECHNOLOGY TRANSFER**

MSE is responsible for preparing and distributing reports for MWTP. These include routine weekly, monthly, quarterly, and annual reports; technical progress reports; and final reports for all MWTP activities. MSE also publicizes information developed under MWTP in local, regional, and national publications. Other means of information transfer include public meetings, workshops, and symposiums.

## **ACTIVITY VI: EDUCATIONAL PROGRAMS**

Montana Tech has developed a post-graduate degree program with a mine waste emphasis. The program contains elements of geophysical, hydrogeological, environmental, geochemical, mining and mineral processing, extractive metallurgical, and biological engineering.

# ORGANIZATIONAL STRUCTURE

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## MANAGEMENT ROLES AND RESPONSIBILITIES

Management of MWTP is specified in the Interagency Agreement. The roles and responsibilities of each organization represented are described below. The MWTP organizational chart is presented in Figure 1.

## ENVIRONMENTAL PROTECTION AGENCY

EPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio, is responsible to EPA's Office of Research and Development for management oversight of project budget, technical direction, schedule, and scope.

## DEPARTMENT OF ENERGY

The Director of the DOE Office of Science and Technology, Office of Environmental Restoration and Waste Management, is the principal DOE representative on the Interagency Agreement Management Committee and provides program review and approval for MWTP. MWTP project management is provided by the Federal Energy Technology Center (FETC), which has line responsibility for applying all applicable DOE regulations to MWTP. MSE is responsible to FETC for management oversight concerning environmental, safety, and health requirements; regulatory actions; and operational conduct of MWTP projects at the MSE Testing Facility in Butte, Montana.

## MSE TECHNOLOGY APPLICATIONS, INC.

MSE, under contract with DOE, is the principal performing contractor for MWTP. The MWTP Program Manager is the point of contact for all mine waste activities. The Program Manager is responsible for Program management and coordination, Program status reporting, funds distribution, and communications.

An MSE project engineer has been assigned to each MWTP project and is responsible to the MWTP Program Manager for overall project direction, control, and coordination. Each project engineer is responsible for implementing the project within the approved scope, schedule, and cost. MSE also provides all staff necessary for completing Activities III and V and oversight of Activities II, III, IV, and VI.

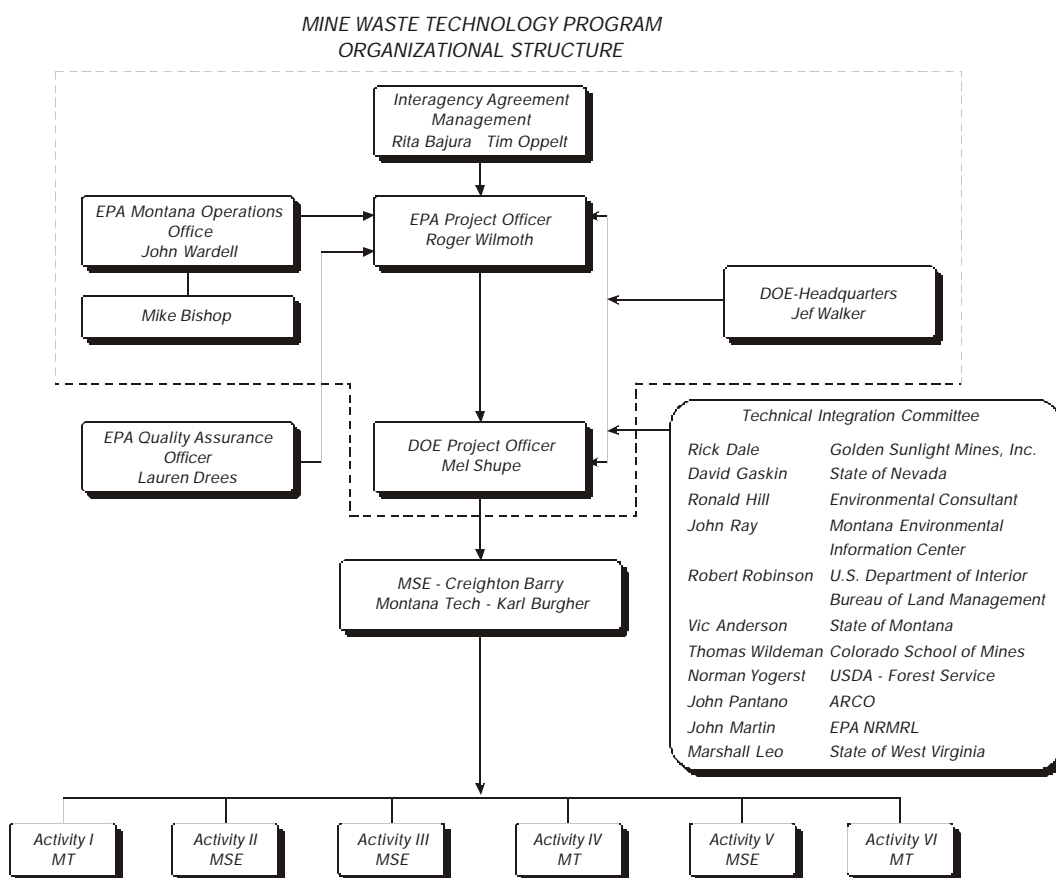
## MONTANA TECH OF THE UNIVERSITY OF MONTANA

As a subcontractor to MSE, Montana Tech is responsible to the MWTP Program Manager for all work performed under Activities I, II, IV, and VI. The responsibility for overall project direction, control, and coordination of the work to be completed by Montana Tech is assigned to the MWTP Montana Tech Project Manager.

## TECHNICAL INTEGRATION COMMITTEE

The Technical Integration Committee is a nine-member committee established to review progress in meeting the goals of MWTP and to alert the Interagency Agreement Management Committee to pertinent technical concerns. The committee

provides information on the needs and requirements of the entire mining waste technology user community and assists with evaluation of technology demonstrations as well as technology transfer. This committee is comprised of representatives from both the public and private sectors.



**Figure 1. MWTP organizational chart.**

# ACTIVITIES

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## DESCRIPTIONS, ACCOMPLISHMENTS, AND FUTURE DIRECTION

This section describes MWTP Activities I through VI and includes project descriptions, major project accomplishments during FY99, and future project direction.

## ACTIVITY I OVERVIEW ISSUES IDENTIFICATION

This activity focuses on documenting mine waste technical issues and identifying innovative treatment technologies. Issues and technologies are screened and prioritized in volumes related to a specific mine waste problem/market.

Following completion of a volume, appendices are prepared. Each appendix links a candidate technology with a specific site where such a technology might be applied. The technology/site combinations are then screened and ranked.

### Technical Issue Status

The status of the volumes approved for development includes:

- Volume 1, Mobile Toxic Constituents—Water and Acid Generation, complete.
- Volume 2, Mobile Toxic Constituents—Air, complete.
- Volume 3, Cyanide, complete.
- Volume 4, Nitrate, complete.
- Volume 5, Arsenic, complete.
- Volumes 1-5 Summary Report, complete.
- Volume 6, Pyrite, complete.

- Volume 7, Selenium, complete.
- Volume 8, Thallium, complete.
- Volume 9, Pit Lakes, in progress.

The status of the appendices for approved projects includes:

- Volume 1, Appendix A (Remote Mine Site), complete.
- Volume 1, Appendix B (Grouting), complete.
- Volume 1, Appendix C (Sulfate-Reducing Bacteria), complete.
- Volume 3, Appendix A (Biocyanide), complete.
- Volume 4, Appendix A (Nitrate), complete.

## ACTIVITY II OVERVIEW QUALITY ASSURANCE

The objective of this activity is to provide support to individual MWTP projects by ensuring all data generated is legally and technically defensible and that it supports the achievement of individual project objectives. The primary means of carrying out this activity is the quality assurance project plan, which is written for each project. This plan specifies the quality requirements the data must meet, clearly states the project objectives, describes all sampling and measurement activities, and contains standard operating procedures, when applicable. Other functions of this activity include reviewing technical systems, validating data, implementing corrective action, and reporting to project management.

Activity II, Preparing a Generic Quality Assurance Project Plan, was completed during FY92 and includes continuing quality assurance activities; therefore, no detailed section for Activity II is included in this report. Specific quality assurance

project plans were prepared for individual projects and are described in the appropriate sections.

## **ACTIVITY III OVERVIEW FIELD DEMONSTRATIONS**

The objective of this activity is to demonstrate innovative and practical remedial technologies at selected waste sites, a key step in proving value for widespread use and commercialization.

Technologies and sites are selected primarily from the prioritized lists generated in the Volumes from Activity I, or they may be a scaleup from bench-scale experiments conducted under Activity IV.

### **ACTIVITY III, PROJECT 3: SULFATE-REDUCING BACTERIA DEMONSTRATION**

#### **Project Overview**

Acid generation typically accompanies sulfide-related mining activities and is a widespread problem. Acid is produced chemically, through pyritic mineral oxidation, and biologically, through bacterial metabolism. This project focuses on a source-control technology that has the potential to significantly retard or prevent acid generation at affected mining sites. Biological sulfate reduction is being demonstrated at an abandoned hard-rock mine site where acid production is occurring with associated metal mobility.

#### **Technology Description**

For aqueous waste, this biological process is generally limited to the reduction of dissolved sulfate to hydrogen sulfide and the concomitant oxidation of organic nutrients to bicarbonate. The particular group of bacteria chosen for this demonstration, sulfate-reducing bacteria (SRB), require a reducing environment and cannot tolerate aerobic conditions for extended periods. These bacteria require a simple organic nutrient.

This technology has the potential to reduce the contamination of aqueous waste in three ways. First, dissolved sulfate is reduced to hydrogen

sulfide through metabolic action by the SRB. Next, the hydrogen sulfide reacts with dissolved metals forming insoluble metal sulfides. Finally, the bacterial metabolism of the organic substrate produces bicarbonate, increasing the pH of the solution and limiting further metal dissolution.

At the acid-generating mine site chosen for the technology demonstration, the Lilly/Orphan Boy Mine near Elliston, Montana, the aqueous waste contained in the shaft is being treated by using the mine as an in situ reactor. An organic nutrient was added to promote growth of the organisms. This technology will also act as a source control by slowing or reversing acid production. Biological sulfate reduction is an anaerobic process that will reduce the quantity of dissolved oxygen in the mine water and increase the pH, thereby, slowing or stopping acid production.

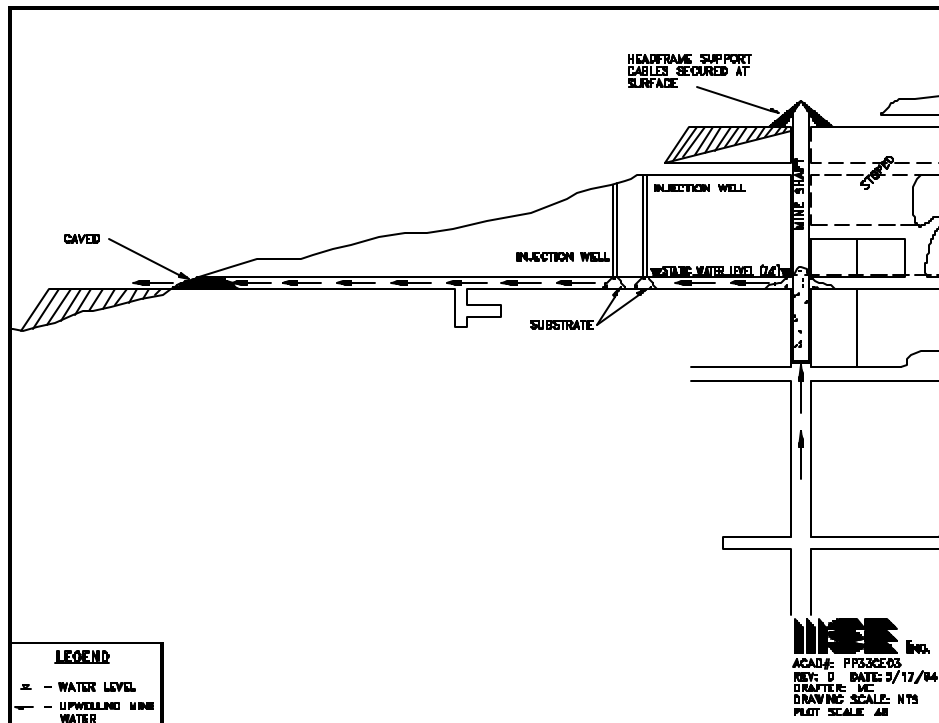
The shaft of the Lilly/Orphan Boy Mine was developed to a depth of 250 feet and is flooded to the 74-foot level. Acid mine water historically discharged from the portal associated with this level.

Pilot-scale work at the MSE Testing Facility in Butte was performed in FY94 prior to the on-set of the field demonstration. The objective of these tests was to determine how well bacterial sulfate reduction lowers the concentration of metals in mine water at the shaft temperature (8 °C) and pH (3).

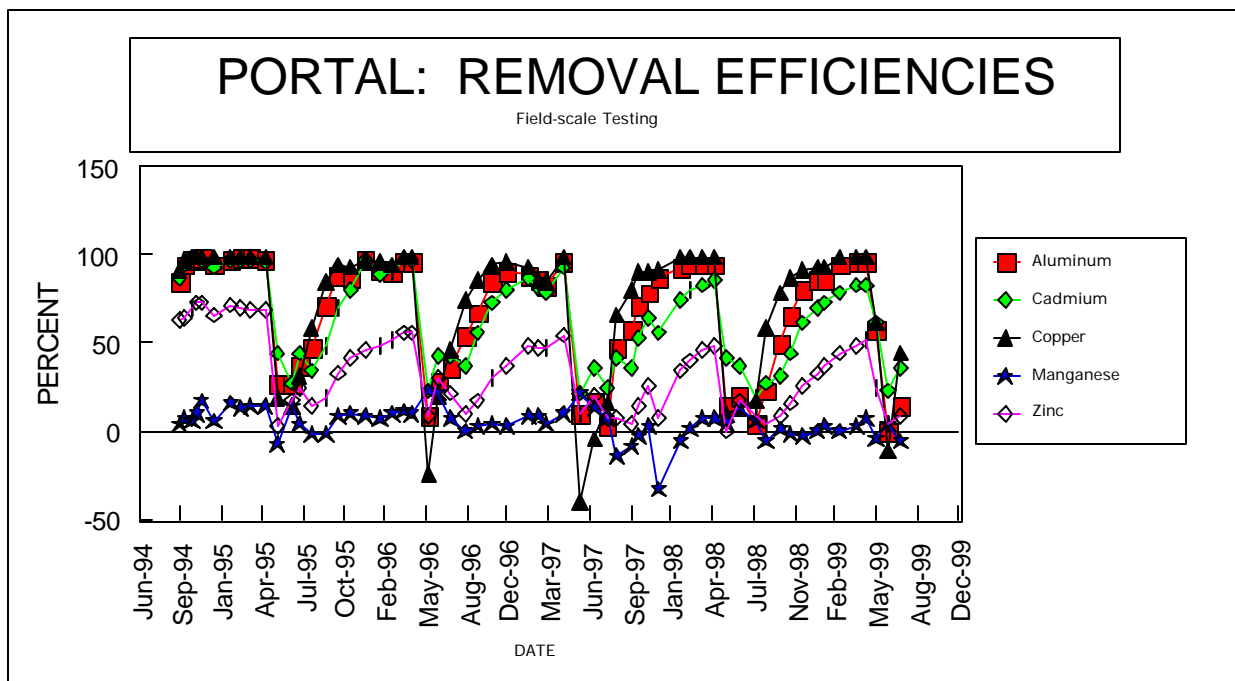
#### **Status**

During FY99, the field demonstration was again monitored on a regular basis. Figure 2 presents a cross-section of the mine and technology installation.

During the past year of monitoring, the data generally demonstrated a decrease in metals concentrations (see Figure 3), with the exception of manganese which SRBs do not effectively remove. An increase in metals was observed during spring runoff as occurred in prior years; however, the levels decreased when flow rates returned to normal. Monitoring of the field demonstration will continue for at least a total of 6½ years.



**Figure 2. Cross-section of the Lilly/Orphan Boy Mine and the technology installation.**



**Figure 3. Metal removal efficiency at the Lilly/Orphan Boy Mine.**



## **ACTIVITY III, PROJECT 8: UNDERGROUND MINE SOURCE CONTROL**

### **Project Overview**

A significant environmental problem at abandoned underground mines occurs when the influx of water contacts sulfide ores and forms acid and metal-laden mine discharge. The Underground Mine Source Control technology was selected to demonstrate that select materials can be used to reduce and/or eliminate the influx of water into the underground mine system; thus, forming an impervious barrier resulting in a reduced, long-term, environmental impact caused by the abandoned mine.

### **Technology Description**

Groundwater flow is the movement of water through fractures, fissures, or intergranular spaces in the earth. With proper application, emplacement of source control materials can inhibit or eliminate this flow.

For this demonstration, a selected source control material will be injected into the fracture system that intercepts the underground mine workings. Some of the fractures are naturally occurring, others were the result of blasting used to further advance the mine workings.

By injecting a source control material, underground pathways (fractures) will be sealed, and an impervious groundwater barrier will be formed. Materials testing will be performed to determine which source control material will be selected. The material will have to be acid resistant, economical, and have rheological properties. As a result, the source control material will offer a potentially long-term solution to acidic and metal-laden water drainage problems.

The demonstration consists of three phases: 1) extensive site characterization; 2) source control materials testing; and 3) source control material emplacement in the underground mine workings.

Phase One consisted of site characterization studies, including hydrogeological, geological, geochemical, and geophysical information directly related to the mine and its past operational procedures.

Phase Two encompasses the source control materials testing. Approximately 40 materials were tested per ASTM methods for acid resistiveness, shear strength, plasticity, compressive strength, compatibility, and viscosity. When compared to a cement-based source control material, the selected material will offer the following advantages: greater retention of plasticity; less deterioration due to the acidic conditions and during rock movement; and better rheological characteristics.

Phase Three consisted of source control material(s) emplacement and yearly monitoring. The material is injected into boreholes at the specified intervals using packers to ensure the material is placed into the proper fracture system.

### **Status**

The project site selected for the demonstration project is the Miller Mine located near Townsend, Montana. This site was selected because the underground workings were accessible, it had a point-source discharge into the underground workings, the slightly acidic inflow is laden with heavy metals, and the inflow could be potentially controlled using the source control technology.

Phase One was completed in March 1999, and the information was used in the definitive design phase of the project. Phase Two was performed at MSE and was finalized during March 1999. Phase Three, the field emplacement, was initiated during August 1999.

## **ACTIVITY III, PROJECT 10: SURFACE WASTE PILES—SOURCE CONTROL**

### **Project Overview**

Surface waste piles from mining operations were historically placed in drainage basins in front of the haulage tunnel. Surface water in the drainage, discharge from the mine, and precipitation usually contacted the waste pile. The water comes in contact with the sulfide ore in the pile and infiltrated through the pile, where acid forms and the water becomes metal-laden. This water percolates from the toe of the pile and flows into the closest surface water. By injecting source control materials strategically in the surface waste pile, there will be a decrease in waters infiltrating through the pile, thereby, decreasing the environmental impact. This technology will be applied in situ, meaning that the pile will be stabilized in place and not excavated and moved to another location for stabilization.

### **Technology Description**

Surface waste piles from historical mining activity, in many cases, consist of broken, low-grade, sulfide ores. When water and oxygen contact the sulfide ores, acid is formed, resulting in increased levels of dissolved metals in the water associated with the pile. The source of the water infiltrating the pile is usually from direct precipitation onto the pile and/or from surface water (i.e., discharge water from a mine adit, stream flow, or in some instances ponded stream/discharge water). Finally, when the water discharges from the surface waste pile, it is acidic and metal-laden, thereby, causing a significant environmental problem.

Usually in such situations, the surface waste pile is excavated and placed in a designed repository. However, this can be expensive, and in some instances, excavation of the pile or construction of a repository is not feasible. In certain instances, in situ placement of a source control material onto the pile is the optimal solution. The source control material is strategically placed into the surface waste pile such that the infiltration of water

through the pile is eliminated or reduced, resulting in a reduction of acidic, metal-laden water.

The demonstration consists of three phases: 1) site characterization; 2) source control materials testing; and 3) field emplacement.

Phase One, site characterization, includes geochemical, geological, hydrogeological, and mineralogical studies that will provide information directly related to the surface waste pile, the mine, the regional water system, and past operational procedures.

Phase Two, source control materials testing, will be done to determine if the selected material is acid resistant, is affected by wet/dry or freeze/thaw cycling, and if it will be impervious once it has been emplaced onto the surface waste pile. The physical characteristics of the surface waste pile material will also be defined in a bench-scale laboratory setting.

### **Status**

The project site for this demonstration is the Peerless Mining Property located south of Rimini, Montana. The site was selected because of its size, hydraulic characteristics, and its water quality. A major factor in the selection of the site was that it had an acidic, metal-laden, point-source discharge flowing from the toe of the surface waste pile, and the upgradient water sources were of better quality and near neutral pH.

Phases One and Two are scheduled to be finalized by March 26, 1999. Phase Three, involving field emplacement, is scheduled to be initiated June 1999.

## **ACTIVITY III, PROJECT 11: CYANIDE HEAP BIOLOGICAL DETOXIFICATION DEMONSTRATION**

### **Project Overview**

Cyanide is used in the mining industry to dissolve precious metals from ore but can contribute to environmental problems. This has led to the development of technologies to degrade cyanide and cyanide complexes in mine wastewater and spent ore heaps. Most of these processes use chemicals to oxidize cyanide and are expensive to operate. Therefore, biological detoxification has been proposed as an alternative to chemical treatment for decommissioning heap leach operations.

### **Technology Description**

This project demonstrated four biological technologies. Project objectives were to:

- reduce the concentration of the effluent weak acid dissociable (WAD) cyanide to meet National and State regulatory standards within a reasonable period;
- determine final effects of biological treatment on related discharge parameters (pH, sulfates, nitrates, metals, and gold recovery); and
- determine technology cost as compared to conventional detoxification methods.

Operation of the column testing began on December 3, 1998, and operated 158 days until May 17, 1999.

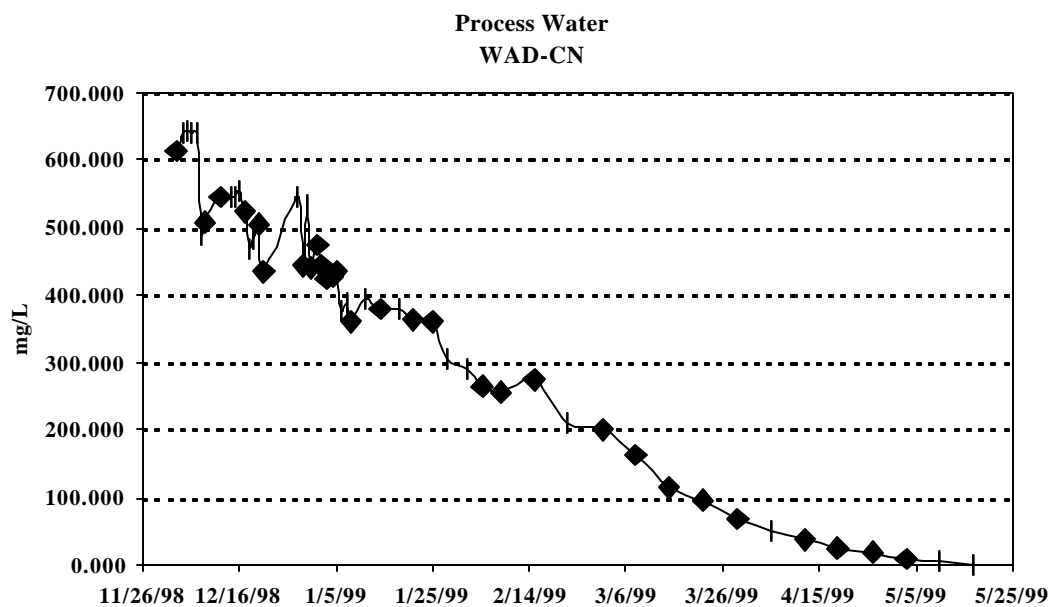
The standard hydrogen peroxide rinse column was demonstrated to have the highest WAD cyanide degradation rate as the regulatory limit of < 0.2 milligrams per liter was reached in 36 days. The process rinse water column showed a cyanide degradation curve of approximately one-third as high as the hydrogen peroxide rinse column.

Three of the biological columns demonstrated were slightly quicker than the process rinse water and were approaching the regulatory limit at termination of the demonstration. However, the fourth technology provider reached the regulatory limit in 151 days.

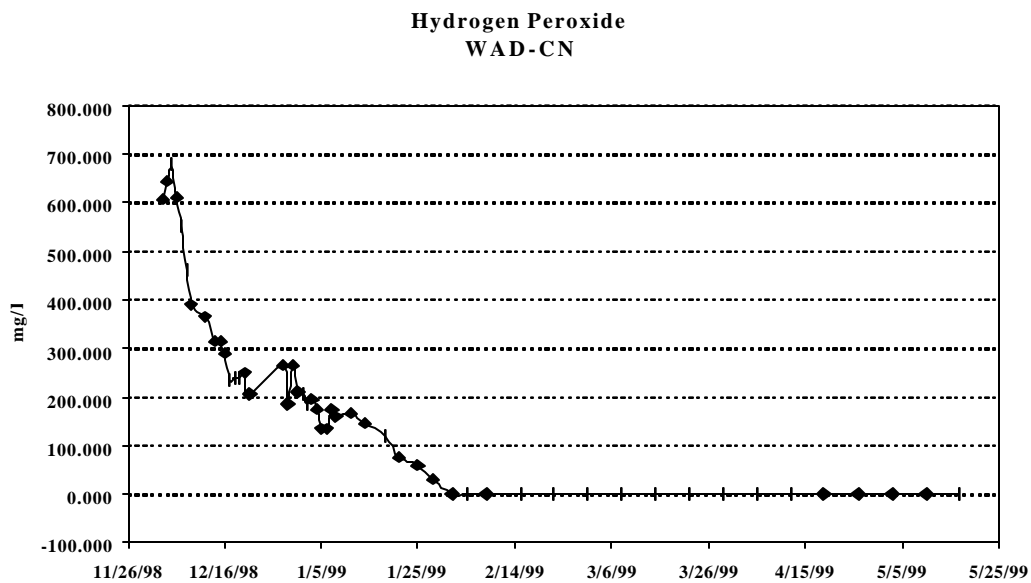
Figures 4 through 9 show WAD cyanide degradation in the six columns.

### **Status**

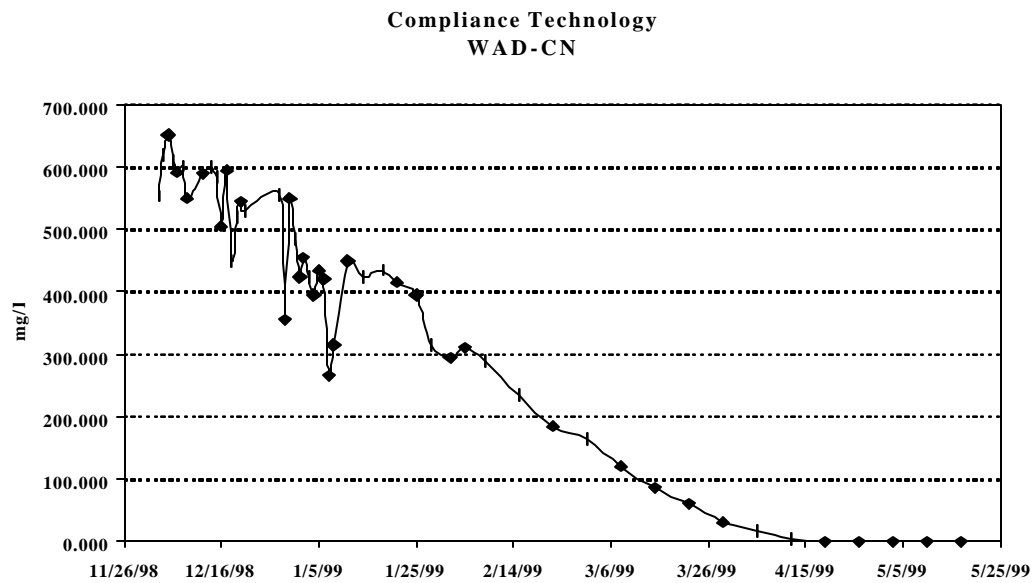
The technology demonstration was completed in May 1999. The final report is scheduled for completion early in 2000.



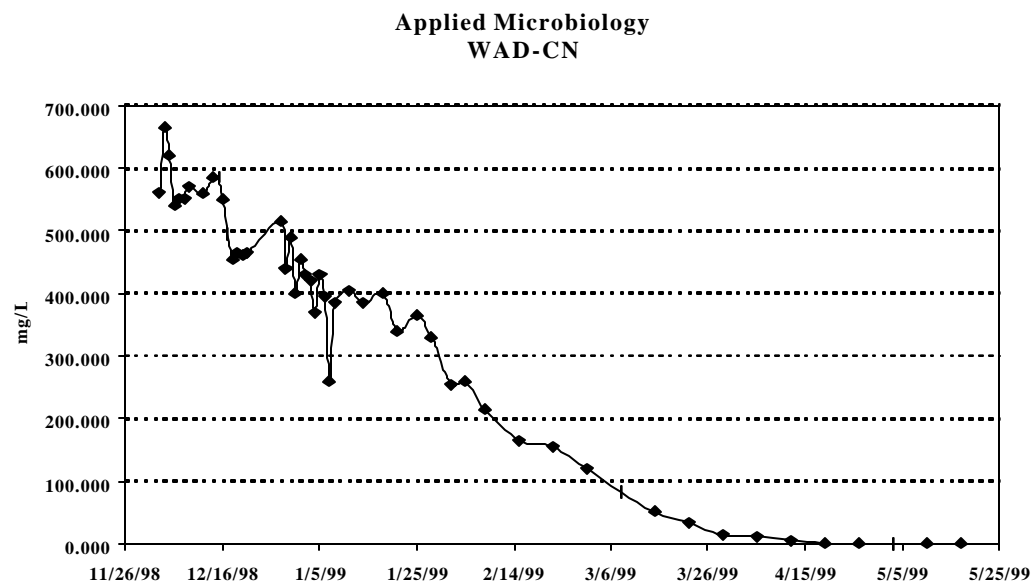
**Figure 4. Process water rinse WAD cyanide.**



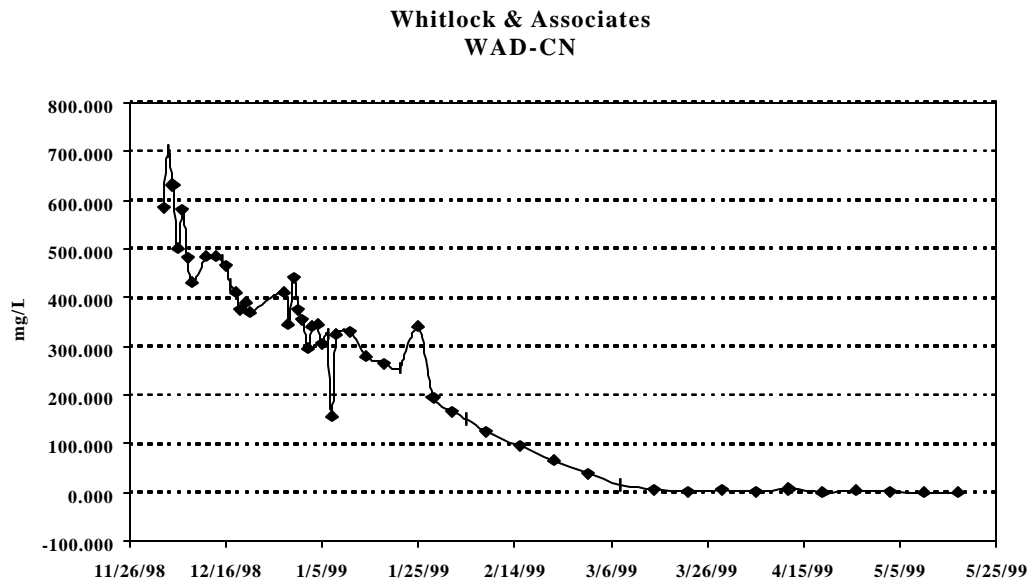
**Figure 5. Hydrogen peroxide rinse WAD cyanide.**



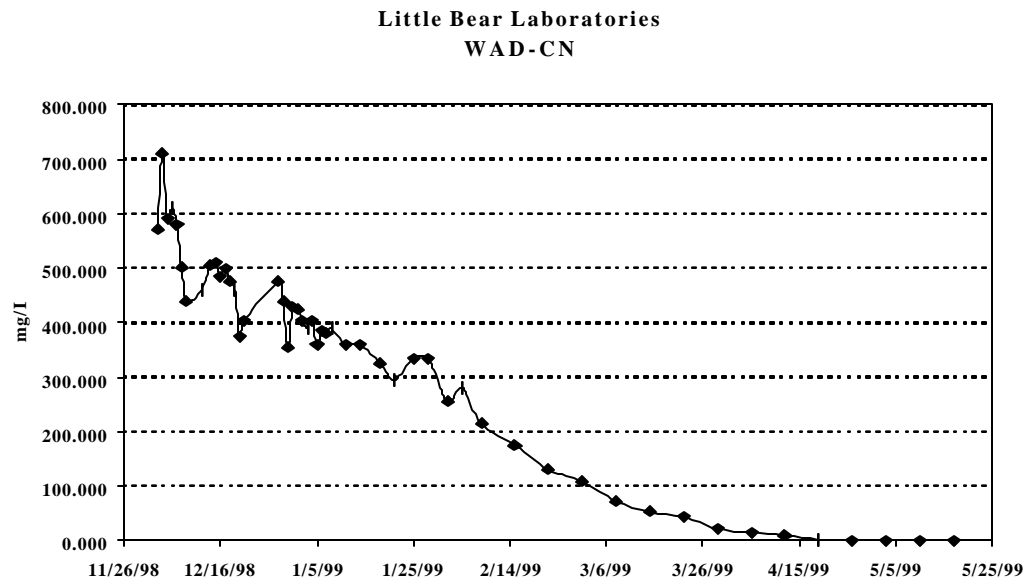
**Figure 6. Compliance Technology WAD cyanide.**



**Figure 7. Applied Microbiology and Biotechnology WAD cyanide.**



**Figure 8. Whitlock and Associates WAD cyanide.**



**Figure 9. Little Bear Laboratories WAD cyanide.**

## ACTIVITY III, PROJECT 12: SULFATE-REDUCING BACTERIA REACTIVE WALL DEMONSTRATION

### Project Overview

Thousands of abandoned mine sites in the Western United States impact the environment by discharging acid mine drainage (AMD) to surface water or groundwater. Acid mine drainage is formed when sulfide-bearing minerals, particularly pyrite, exposed by mining activities to oxygen and water, engage in a chemical reaction that results in an increased acidity of the water (lowered pH), and increased concentration of dissolved metals and sulfate.

At many abandoned mine sites in the West, conventional treatment strategies for AMD (e.g., lime neutralization) are not feasible because of the remoteness of the mine locations, insomuch as a lack of a power source and limited site accessibility in winter. Sulphate-reducing bacteria (SRB) are capable of reducing the sulfate to sulfide, decreasing the load of dissolved metals in the effluent by precipitating metals as sulfides, and increasing the pH of the effluent. To demonstrate the feasibility of using SRB passive technology for mitigation of AMD emanating from the toe of a waste rock pile, three bioreactors were built at the abandoned Calliope Mine site located near Butte, Montana.

### Technology Description

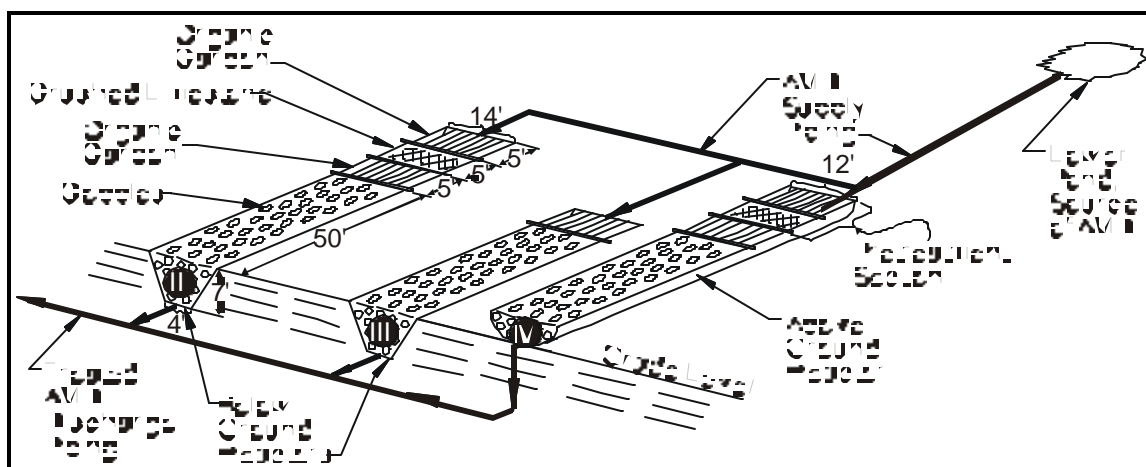
The abandoned Calliope Mine site includes a collapsed adit discharging water into a large waste rock pile. This relatively good quality water percolates through the mine waste and reappears on the surface (at the toe of the pile) enriched in metals with an average pH of 2.6. This AMD mixes with good quality surface water and accumulates in a pond (lower pond). As a result, the pH of water in the lower pond ranges from 3 to 5.5 depending on the surface water and AMD mixing ratio, which varies seasonally. This low pH water in the lower pond is the target water for the SRB technology demonstration.

Three SRB bioreactors constructed at the Calliope abandoned mine site in the fall of 1998 are approximately 70 feet long, 14 feet wide, and 6 feet high. They are placed in parallel (see Figure 10) downstream from the lower pond, allowing the AMD to be piped to and treated by the respective reactors using gravity flow. The bioreactors were designed to evaluate the SRB technology applied under different environmental conditions.

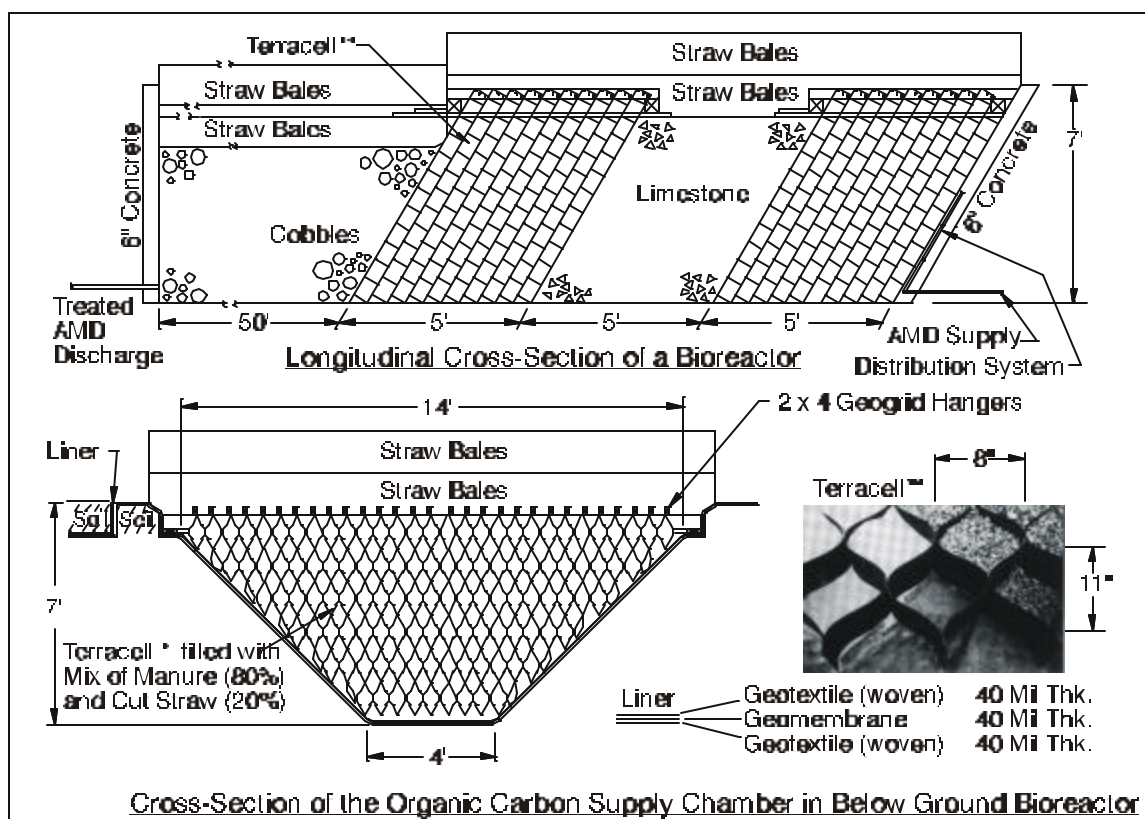
Two bioreactors were placed in trenches. One was constructed above the ground using a 12-foot-wide metal half-culvert to investigate impact of seasonal freezing and thawing on SRB activity. To evaluate the efficiency of the SRB at optimal pH and oxidation-reduction potential ( $E_H$ ), two of the reactors contain a passive pretreatment section to increase pH.

Each reactor is filled with a combination of organic carbon, crushed limestone, and cobbles placed in discrete chambers (see Figures 10 and 11). Each of these media is expected to play a certain role in the treatment train. 1) Organic carbon is bacterial food supply and, because it was provided in the form of cow manure, also the SRB source. 2) For the pretreatment section, a chamber with cow manure was included to lower the  $E_H$  of AMD. 3) Crushed limestone provided buffering capacity to increase the pH of AMD in the pretreatment section. 4) Cobbles placed in the reactive, primary treatment section of the bioreactor constitute stable substrate for bacterial growth.

Chambers filled with organic carbon or limestone are each 5 feet long, whereas, chambers filled with cobbles are 50 feet long. Such dimensions were selected based on the literature review and information acquired through the bench-scale test that was conducted in the MSE laboratory in 1998. Preliminary results of the bench-scale test, at the time of the bioreactor's design, indicated the required residence time in the reactors should range from 3 to 5 days. The bioreactors were sized to secure such a residence time for the flow rate of one gallon per minute through each reactor. Nevertheless, the flow and hydraulic head control systems placed in the bioreactors ensure a much wider range of the residence time.



**Figure 10. Layout of bioreactors.**



**Figure 11. Bioreactor's design.**



The main challenges were to design the organic carbon chambers so the AMD would permeate through the entire cross-sectional area without channeling, and to ensure that the organic substrate did not settle. These goals were achieved by placing the organic substrate in the cellular containment system assembled of 10 lifts of Terracell™ (see geogrid in Figure 11) that would limit settling (if occurred) of the organic matter to each individual cell. The Terracell™ lifts were positioned at 600 degrees off the horizontal plane to facilitate packing it with the organic substrate and to promote migration of AMD along a wavy-shaped flowline.

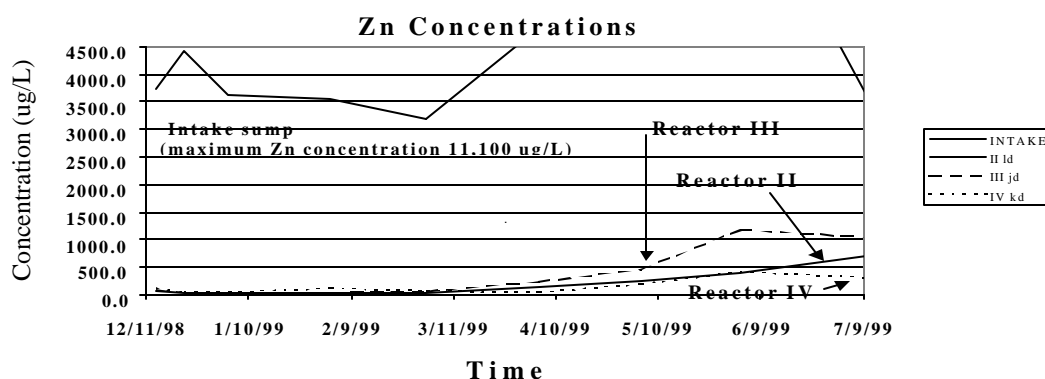
## Status

### Operation of Bioreactors

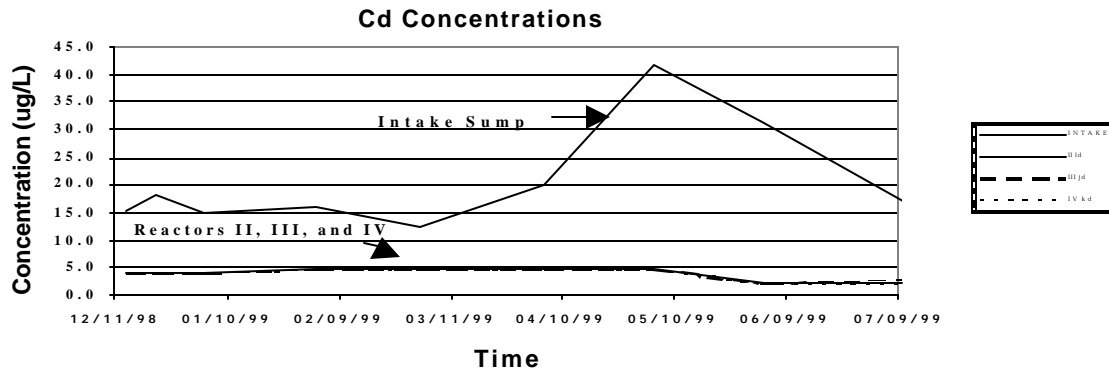
Reactor construction was completed in November 1998, and the reactors have been in operation since December 1999. The operation plan stipulated that the two below-grade reactors (II and III) would flow at the rate of 1 gallon per minute (gpm) and reactor IV would be shut down for the winter to let it freeze full of AMD. After spring thawing, the flow rate of reactor IV would also be 1 gpm. The 1-gpm flow rate allows for approximately a 5½-day residence time of AMD in reactors II and IV and a 4½-day residence time in reactor III.

The performance of each reactor has been monitored by monthly sampling of the influent (AMD) and effluent, and continuous monitoring of selected parameters using appropriate sensors and data loggers. Water samples have been analyzed for sulfate; alkalinity; SRB count; heterotrophic bacteria count; dissolved oxygen;  $E_H$ ; and metals that include aluminum, zinc, cadmium, copper, iron, manganese, and cadmium. Temperature, pH, water level, and flow rate were recorded at 4-hour intervals by two data loggers. Selected results of the reactors performance are shown in Figures 12 through 14.

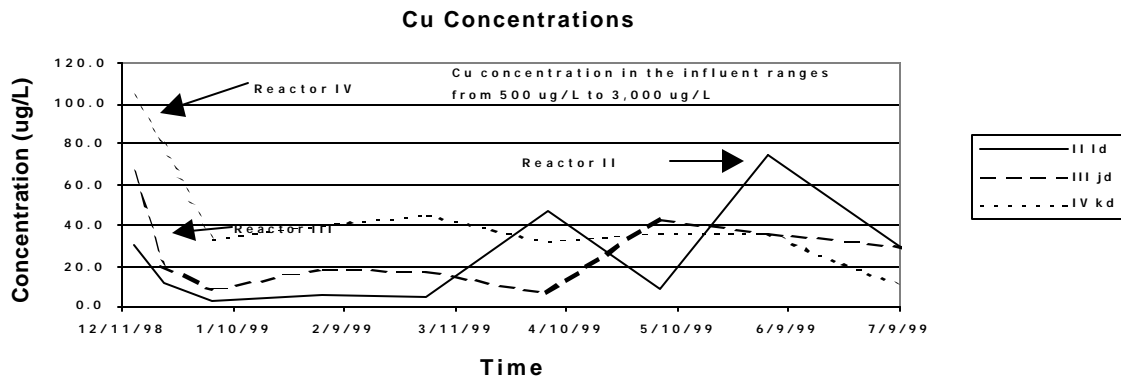
The first 8 months of operation can largely be described as a period in which the microbial populations were becoming established within the reactors. It should be noted that the reactors were initiated in the winter when temperatures were not ideal for microbial growth. Much of the metals removal observed during this period can be attributed to adsorption. Once sorption sites fill and SRB populations become established, many metals [e.g., zinc (Figure 12), cadmium (Figure 13), and copper (Figure 14)] were removed through SRB activity precipitating as metal sulfides. Aluminum seems to be removed from AMD by precipitating as hydroxide. Precipitation of other metals like manganese and iron is not enhanced by the environment of low  $E_H$  created in bioreactors.



**Figure 12. Concentration of zinc in AMD and reactor effluents.**



**Figure 13. Concentration of cadmium in AMD and reactor effluents.**



**Figure 14. Concentration of copper in reactor effluents.**

## ACTIVITY III, PROJECT 12A CALLIOPE MINE INTERNET MONITORING SYSTEM

### Project Overview

This project entails the design and construction of a state of the art Internet monitoring system at the Calliope Mine site. This monitoring system will be linked to the MSE Testing Facility in Butte, Montana, via a cellular modem connection. Data from the remote mine site will be polled by a dedicated personal computer (PC) located at the MSE Testing Facility.

### Technology Description

The polling PC will run software designed for existing data loggers. The new software will have the ability to automatically call the remote cell phone once a day to retrieve stored information on the data loggers. Once data has been retrieved, it will be transferred to a web server and stored in an industrial database. The Internet web server will have a dedicated frame relay or wireless connection out to the World Wide Web (see Figure 15). An Internet service provider will be obtained to allow this connection as well as provide ample internet protocol addresses and domain names for the web site. Web screens will be designed to allow anyone

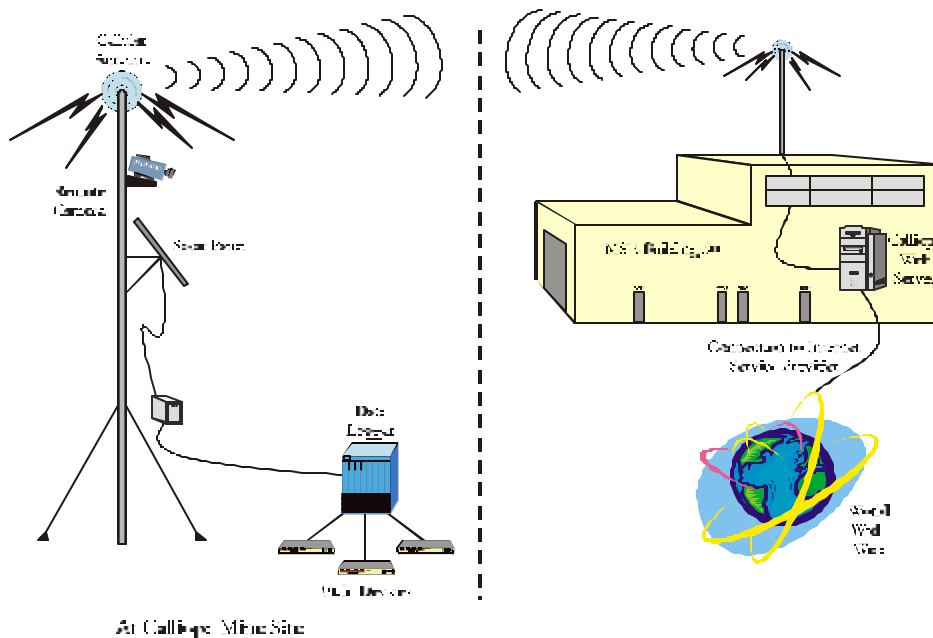
with a PC and Internet access to view information retrieved from the Telemetry System (see Figure 16). The screens will allow viewing of historical data as well as trending of data. Some information may be password protected for security purposes.

This project will also include the task of upgrading the existing data logger's battery storage capacity. The existing In Situ Hermit 3000 Data Loggers do not have enough battery storage to run loggers and existing instruments at specific sample rates. This problem is also compounded by the fact that additional pH instruments are to be installed in the near future. The loggers have failed due to dead onboard batteries in unacceptable time periods. The new design will consider existing data loggers, current and future instruments, as well as the new Telemetry System. The total system will be evaluated and designed to provide ample power for all equipment. The new system will be battery powered and charged from the use of Photovoltaic Solar Collection Panels.

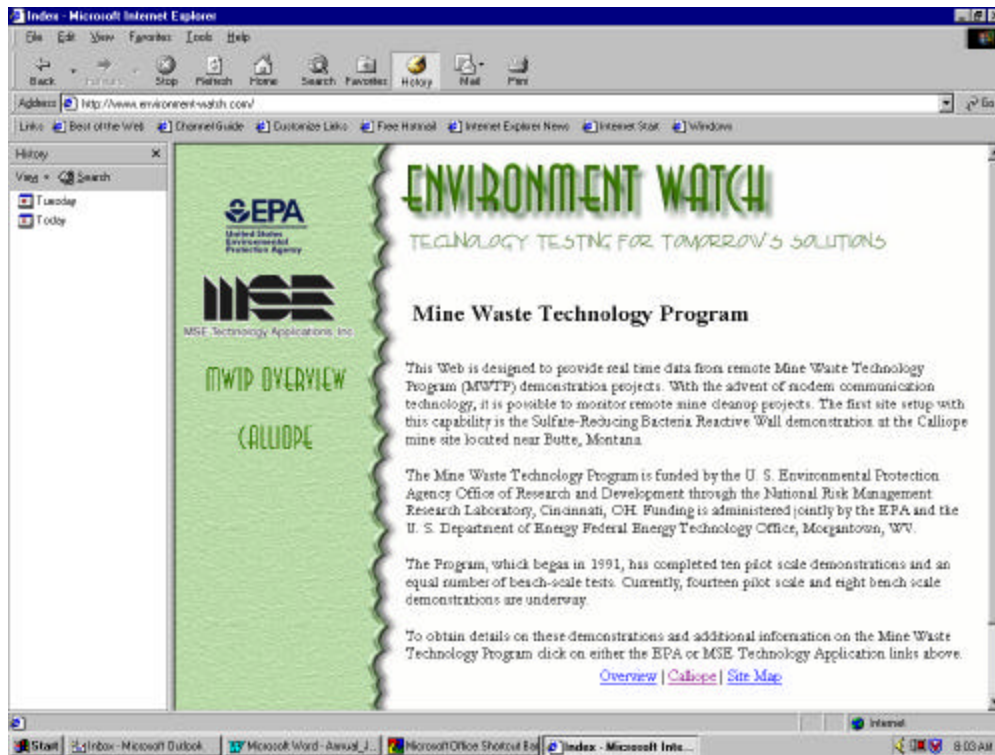
The installation of this new Internet web server will provide ample capacity for future Mine Waste Technology Program projects. These projects could also benefit by using the same web server to post information onto the World Wide Web.

## Status

As of September 30, 1999, the project was 10% complete. The web server was procured, configured, and installed. The dial-up cell phone telemetry system has been back ordered by the manufacture. The delay of equipment set the project behind slightly. It is anticipated that with the delays the telemetry system will be installed and completed by April 15, 2000.



**Figure 15. Calliope Mine Internet Monitoring System.**



**Figure 16. Calliope Mine web server home page "environment-watch.com."**

## ACTIVITY III, PROJECT 13: HYDROSTATIC BULKHEAD WITH SULFATE-REDUCING BACTERIA

### Project Overview

The technology addressed in this project is designed to reduce or eliminate acid drainage from underground mine workings. The demonstration is intended to illustrate the feasibility of using an innovative source control technology in a way that provides increased stability, structural applicability and continuity, and economical comparability to the conventional methods of acid drainage treatment used by the mining and waste industries. The technology used for this demonstration will be stable in the environment.

### Technology Description

The technology selected for this demonstration is a combination hydrostatic bulkhead constructed of

concrete and rebar, with a colony of sulfate-reducing bacteria (SRB) placed behind the bulkhead. The acid drainage in the mine will be treated by raising the pH of the contained water behind the bulkhead causing metals to be removed. The metals removal processes that can occur include adsorption and complexation of metals by organic substrates, biological sulfate reduction followed by precipitation of metals as sulfides, precipitation of ferric and manganese oxides, adsorption, adsorption of metals by ferric and manganese hydroxides, and filtration of suspended and colloidal materials. Biological sulfate reduction, however, should be the predominant metal removal mechanism.

### Status

The search for a suitable site resumed after abandonment of the project at the Silver Dyke Mine east of Neihart, Montana. The native rock in the tunnel at the Silver Dyke proved to be unsuitable for installing a bulkhead. Hard and competent rocks are required to ensure the integrity of a bulkhead installation.

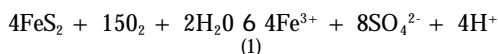
Negotiations are in progress with the American Smelting and Refining Company (ASARCO) to install a SRB colony behind a bulkhead to be constructed by ASARCO at the Triumph Mine in Triumph, Idaho.

## ACTIVITY III, PROJECT 14: BIOLOGICAL COVER DEMONSTRATION

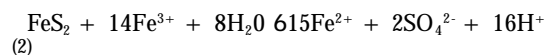
### Project Overview

Acidic, metal-laden waters draining from abandoned mines have a significant environmental impact on surface waterways throughout the nation and the world. Specifically, the State of Montana has identified more than 20,000 abandoned mine sites, on both public and private lands, resulting in more than 1,300 miles of streams experiencing pollution problems.

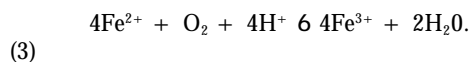
This problem arises from waste rock containing sulfide minerals and lacking acid-consuming carbonate minerals. Sulfide minerals, such as pyrite ( $\text{FeS}_2$ ) are oxidized to form sulfate when water-containing oxygen infiltrates tailings. This process can be described by the following reaction:



The activity of bacteria, such as *Thiobacillus ferrooxidans*, which are capable of oxidizing inorganic sulfur compounds, greatly accelerates this reaction. The ferric iron ( $\text{Fe}^{3+}$ ) produced in the above reaction also contributes to pyrite oxidation:



*T. ferrooxidans* is also capable of oxidizing ferrous iron ( $\text{Fe}^{2+}$ ) produced in the above reaction:



Thus, the ferric iron is regenerated and capable of oxidizing more pyrite. The key to breaking this cycle is preventing the initial oxidation of pyrite.

Bound with iron, the sulfur in pyrite is unable to participate in the microbially catalyzed reactions that cause acid generation. Prevention of oxygen infiltration into tailings then is necessary to prevent oxidation of pyrite and subsequent acid generation. An innovative method to prevent oxygen transport into tailings is the construction and maintenance of a biologically active barrier on the surface of the tailings. This barrier is made up of aerobic and facultative bacteria (bacteria that are capable of living under different conditions) that use dissolved oxygen in the infiltrating water, therefore, maintaining the reducing conditions that are necessary for pyrite to remain bound in mineral form.

MSE and researchers at the Center for Biofilm Engineering at Montana State University are investigating the microbial processes involved with establishing and maintaining subsurface and near surface microbial barriers for hydraulic control and microbially catalyzed reactions. Biobarrier technology has been successfully tested in laboratory and field-scale systems where permeability reductions of up to five orders of magnitude were achieved. These experimental systems have proven, likewise, that biobarriers constructed of aerobic or facultative organisms can successfully remove oxygen from infiltrating water to trace levels.

This biological barrier demonstration project is the fourteenth project to be conducted by MSE as part of the Mine Waste Technology Program (MWTP). By conducting this demonstration, MWTP is illustrating the ability of the microbial biomass to reduce the permeability of mine tailings and remove oxygen from infiltrating water, thus, reducing the generation of AMD. This technology promises to be a cost-effective approach for the stabilization and remediation of acid generating abandoned mine tailings.

### Technology Description

A solution containing bacteria and low-cost nutrients are applied to the top of the tailings pile to form a biological barrier. Following an incubation period, nutrient solution is periodically applied to further develop the biological barrier. The bacteria to be used will be a consortium of aerobic and facultative heterotrophic bacteria originally derived from the mine tailings to be treated. The oxidation of carbon

compounds in the nutrient mixture by bacteria in the barrier depletes oxygen in the infiltrating water. Furthermore, bacterial cells and associated extracellular polymers occupy free pore space within the tailings matrix, greatly reducing permeability. The reduction in water volume flowing through the tailings and depletion of oxygen as water passes through the barrier will mitigate pyrite oxidation and subsequent acid production. The anaerobic conditions and production of organic acids by fermentative bacteria in the biobarrier may also promote the growth of sulfate-reducing bacteria (SRB). The activity of SRB is desirable in that it consumes acid and stabilizes metals by H<sub>2</sub>S-mediated metal sulfide precipitation. Laboratory-scale experiments have demonstrated that biological barriers are capable of generating conditions suitable for SRB growth.

## Status

The site selected for implementation of this technology is the Mammoth Tailings Site located in the South Boulder Mining District approximately 18 miles from Cardwell, Montana. Two, lined test cells were constructed at the field site in the fall of 1999 and will be monitored to evaluate base-line water quality until the spring of 2000 when the biological barrier treatment will be applied to one of the test cells.

Laboratory tests using tailings samples collected from the Crescent Mine have been completed. These tests demonstrated the ability of the biological barrier treatment to establish and maintain reducing conditions within the tailings. Laboratory tests using tailings from the Mammoth Site are currently underway. Project completion is expected in November 2001.

## ACTIVITY III, PROJECT 15: TAILINGS SOURCE CONTROL

### Project Overview

Processing metallic ores to extract the valuable minerals leaves remnant material behind called

tailings. In the case of sulfide mineral-bearing ores, process tailings often contain large quantities of sulfide minerals that do not meet the economic criteria for extraction. These remnant sulfide minerals are usually pyrites and nonextracted ore minerals, and the exposure of these minerals to air and water often leads to detrimental environmental conditions such as increased sedimentation in surface waters due to runoff events, generation of acid mine drainage, and increased metals loading in surface and groundwaters.

## Technology Description

This project will identify potential source control materials and apply one or more of them at a selected site. The demonstration consists of two phases: 1) site characterization and materials testing; and 2) materials emplacement and long-term monitoring and evaluation.

Phase one consists of the site characterization studies, including hydrogeological, geological, and geochemical information directly related to the tailings impoundment. The materials testing and development will involve testing, evaluation, and formulation of materials for application at the selected site.

Phase two encompasses the application of one or more of the selected materials at the demonstration site and the evaluation of the material versus the original tailings material at the site. Long-term evaluation of the materials will be performed using moisture profiles generated from monitoring equipment.

## Status

Phase one is in the initial stages, the project site selected for this demonstration is the Slaughterhouse Tailings site located west of the historic mining town of Elkhorn, Montana. Material testing is in progress and will be finalized during the second quarter of 1999. Emplacement of source control materials at the selected tailings impoundment is scheduled to be done during the summer of 1999, and the evaluation of the cap will extend through FY00.

## **ACTIVITY III, PROJECT 16: INTEGRATED PASSIVE BIOLOGICAL TREATMENT PROCESS DEMONSTRATION**

### **Project Overview**

This project is demonstrating an integrated passive biological treatment reactor. The objective of this project is to develop technical information on the ability of an integrated passive biological reactor to passively treat and improve water quality at a remote mine site. This technology offers advantages over many acid mine drainage (AMD) treatment systems because it does not require a power source or frequent operator attention. For the purposes of this demonstration, the technology will treat the acidic aqueous waste by removing toxic, dissolved metallic and anionic constituents from the water in situ and increasing the pH so the effluent is near neutral.

### **Technology Description**

The technology uses a series of biological processes for the complete mitigation of AMD by concentrating and immobilizing metals within the reactors and raising the pH of the water. Both anaerobic and aerobic bacteria will be used to mitigate AMD. The bacteria will be fed inexpensive waste products such as feed-lot wastes. The anaerobic bacteria, namely sulfate reducing bacteria (SRB), are a group of common bacteria that are able to neutralize AMD and remove toxic metals. When supplied with sulfate (present in mine water) and a carbon source, SRB produce bicarbonate and hydrogen sulfide gas. Bicarbonate neutralizes AMD while hydrogen sulfide gas reacts with metal ions to precipitate them as insoluble metal sulfides. Aerobic bacteria will be used to mitigate metals, such as iron and manganese, that are not removed satisfactorily by SRB. The result will be an integrated biological system capable of completely and passively mitigating AMD.

The first phase of the project will include field site selection and characterization and laboratory testing. Laboratory testing will be performed to identify design parameters for the field design.

The second phase of the project will include the design and construction of an integrated passive biological treatment system to treat AMD at a selected remote mine site. The system will likely be constructed underground near a discharging mine portal to protect it from climatic conditions at the surface. Organic substrates to nourish the bacteria will be selected and used within the system. To ensure sufficient hydraulic conductivity through the system, appropriate materials will be added to the organic substrate.

### **Status**

This project was initiated at the end of FY98. A mine site was selected for the field demonstration, and bench-scale testing in laboratory columns was initiated. Design and construction of the field application are scheduled to occur in FY00.

## **ACTIVITY III, PROJECT 17: LEAD ABATEMENT DEMONSTRATION**

### **Project Overview**

The foremost cause of childhood lead poisoning in the United States is the ingestion of lead-based paint found in older housing. The overall objective of this demonstration was to obtain cost and performance data on an innovative set of technologies capable of removing lead-based paint from interior decorative wood in residential housing with minimal damage to the underlying substrate and no residual hazardous waste.

## Technology Description

The technologies evaluated included the paint removal system PR-40/LEADX™/PR-40AFX™ and a carbon dioxide blasting technology.

The paint removal system PR-40/LEADX™/ PR-40AFX™ was demonstrated to effectively remove lead-based paint and/or lead-based varnish from interior decorative wood with minimal apparent damage to the wood substrate within certain operational limitations. The product proved effective when previous paint/varnish layers were between six to eight layers. Other wall coverings beneath the paint surface (i.e., wallpaper or wall texturing) further impacted penetration of PR-40/LEADX™/PR-40AFX™.

The carbon dioxide blasting technology was effective in removing the lead-based paint only in areas where PR-40/LEADX™/PR-40AFX™ had achieved full penetration of all paint layers.

However, the blasting technology produced an unsatisfactory erosion of soft wood from the target wood leaving the surfaces feathered and/or gouged. Figures 17 through 19 show paint removal through repainting.

## Status

The technology demonstration was completed in February 1999. The final report is available.



**Figure 17. Removal of product and paint using pelletized dry ice blasting.**





***Figure 18. Living room bay window molding showing nearly complete paint removal down to bare wood.***



***Figure 19. Living room bay window following repainting with latex paint.***

## ACTIVITY III, PROJECT 18: GAS-FED SULFATE-REDUCING BACTERIA BERKELEY PIT WATER TREATMENT

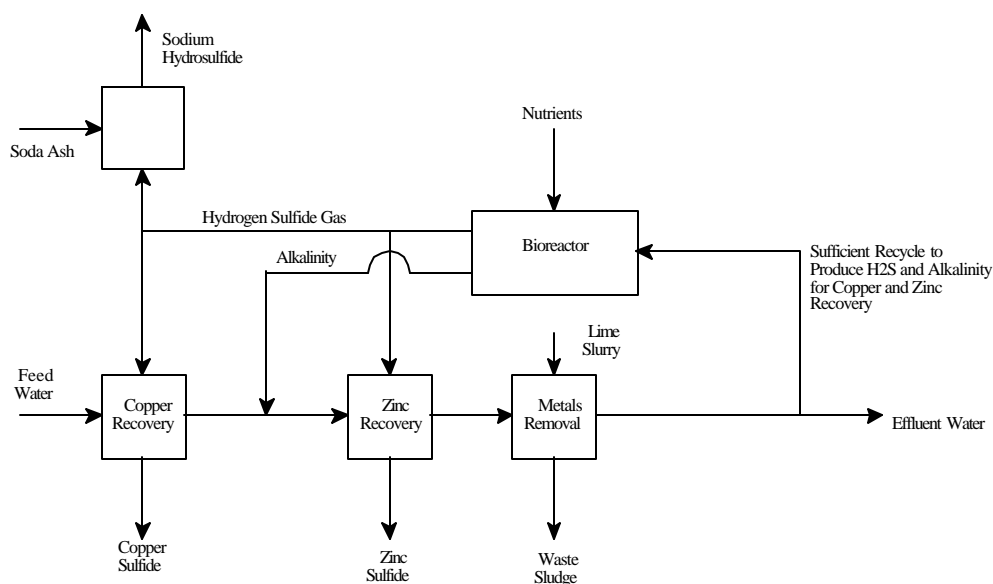
### Project Overview

Sulfate-reducing bacteria (SRB) are a well-known, effective method for treating acid rock drainage. With the proper conditions of solution temperature and oxidation/reduction potential, and with suitable nutrients available to the SRB, sulfate is electrochemically reduced to sulfide, which forms insoluble precipitates with many metals. In addition, alkalinity is produced that serves to raise the solution pH. Previous and current Mine Waste Technology Program projects have successfully demonstrated SRB in remote locations with the goal of providing improved water quality at low cost. Advances have been made in engineered systems utilizing SRB, particularly in the area of providing cheap nutrients to the bacteria, which significantly enhance overall system economics. These advances increase the possibility of utilizing SRB as part of an acid mine drainage (AMD) treatment system in

which selected metals are separated and recovered for resale, offsetting overall treatment costs. This project will demonstrate and evaluate a process with the potential to profitably recover copper, zinc, and sodium hydrosulfide from Berkeley Pit water.

### Technology Description

Biomet Mining Corporation of Vancouver, British Columbia, has patented a method utilizing combustion products from natural gas as nutrients for SRB, called the Biosulfide process. This cheap source of nutrients has enabled Biomet to show favorable economics in recovering copper and zinc products from AMD at pilot-scale at several locations in North America. Copper is recovered directly as copper sulfide using hydrogen sulfide gas produced by SRB. Following a pH adjustment using the alkalinity produced by the SRB, hydrogen sulfide gas is used to recover zinc as zinc sulfide. Other products, including sodium hydrosulfide and sulfuric acid, can be produced with downstream processing if the economics at a specific location are favorable. A generalized schematic of the process is shown in Figure 20.



**Figure 20. Biomet Mining Corporations's Biosulfide Process.**

## Status

Bench-scale miniplant testing began at MSE's facility in October 1998. Biomet performed laboratory tests to determine initial pH and oxidation/reduction potential conditions for copper and zinc separation/recovery from September to November 1998. Biomass development was performed at MSE with the pilot-scale system between December 1998 and May 1999. Biomet moved the pilot system to the Berkeley Pit in May 1999, and MSE had virtually no involvement in the project after that time due to budgetary constraints. Pilot-scale operation continued at the Berkeley Pit until September 1999, at which time the pilot system was shut down with tentative plans to restart in April 2000. Pilot-scale operation was plagued with operational problems, particularly related to the performance and reliability of the natural gas burner and to the sulfate reduction performance of the bacteria. MSE initiated termination of their support of the project in December 1999. Biomet still hopes to run the pilot system at the Berkeley Pit during the summer of 2000.

## ACTIVITY III, PROJECT 19: SITE IN SITU MERCURY STABILIZATION TECHNOLOGIES

### Project Overview

This demonstration project will be conducted in conjunction with EPA's Superfund Innovative Technology Evaluation (SITE) Demonstration Program. As part of the overall project, MSE will be responsible for conducting technology assessment activities.

The Sulphur Bank Mine in Clear Lake, California, has been identified as the source of mercury contaminated mining wastes for this demonstration project. This abandoned mine is located in a geothermal active area. This site was historically mined for mercury and sulfur using both underground and open pit mining methods. The site consists of approximately 120-acres that contains mine tailing, rock piles, and a pit lake.

The mine tailings are located upgradient and extend into and along the shoreline of Clear Lake. The development of an in situ mercury treatment/stabilization technology could be used to address the significant mercury contamination problems at this site.

### Technology Description

The main objective of this effort is to demonstrate the effectiveness of various technologies for the in situ treatment/stabilization of mercury contaminated mining materials. This technology demonstration project will allow the Mine Waste Technology Program to conduct comparative demonstrations of various mercury treatment/stabilization technologies. The information from this project will serve to provide valuable data for abandoned mine remediation projects. In addition, it will be determined if any of the tested technologies are practical for field applications.

Sulfide precipitation is the best-demonstrated available technology for mercury stabilization or removal from aqueous liquids. Several methods of sulfide precipitation are applicable, which include solutions of sodium hydrosulfide, hydrogen sulfide gas, and sulfate-reducing bacteria. Several technologies will be demonstrated, which may include biomineralization, chemical/physical treatment, capping, grouting, and redox reduction. Other technologies may be tested as part of this demonstration if they are identified to be applicable.

### Status

The technology demonstration is pending identification of appropriate testing material from the Sulfur Bank Mine site by the SITE Program.

## ACTIVITY III, PROJECT 20: SELENIUM REMOVAL/TREATMENT ALTERNATIVES

### Project Overview

The purpose of the Selenium Removal/Treatment Alternatives Demonstration Project is to: 1) evaluate the performance of the selected processes in the field using selenium-bearing water; 2) evaluate the affect of competing ions on selenium removal efficiency; and 3) determine full-scale capital and operating costs of the processes being demonstrated.

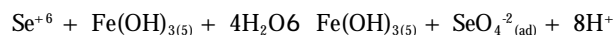
The following selenium removal technologies will be demonstrated: 1) EPA's Best Demonstrated Available Technology (BDAT) for treating selenium-bearing waters and coprecipitation of selenium using ferrihydrite as optimized by MSE; 2) catalyzed cementation technology developed by MSE; 3) biological reduction of selenium technology developed by Applied Biosciences Corporation of Park City, Utah; and 4) enzymatic reduction of selenium technology developed by Applied Biosciences Corporation of Park City, Utah.

The project is being conducted at Kennecott Utah Copper Corporation. The influent water used for the demonstration is a groundwater containing approximately 2 ppm selenium. The primary objective is to reduce the concentration of dissolved selenium in the effluent waters to a level under the National Primary Drinking Water Regulation Limit for selenium of 50 ppb established by EPA.

### Technology Description

#### *Ferrihydrite Precipitation*

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface is the BDAT for treating selenium-bearing waters. For the coprecipitation to occur, ferric ion ( $\text{Fe}^{+3}$ ) must be present in the water. Selenate ( $\text{Se}^{+6}$ ) is removed from the water at pH below 4. The chemical reaction for ferrihydrite precipitation of selenium is:



The ferrihydrite precipitation process and the catalyzed cementation process are shown together in Figure 21. (The ferrihydrite precipitation process is shown in the upper half of the drawing.)

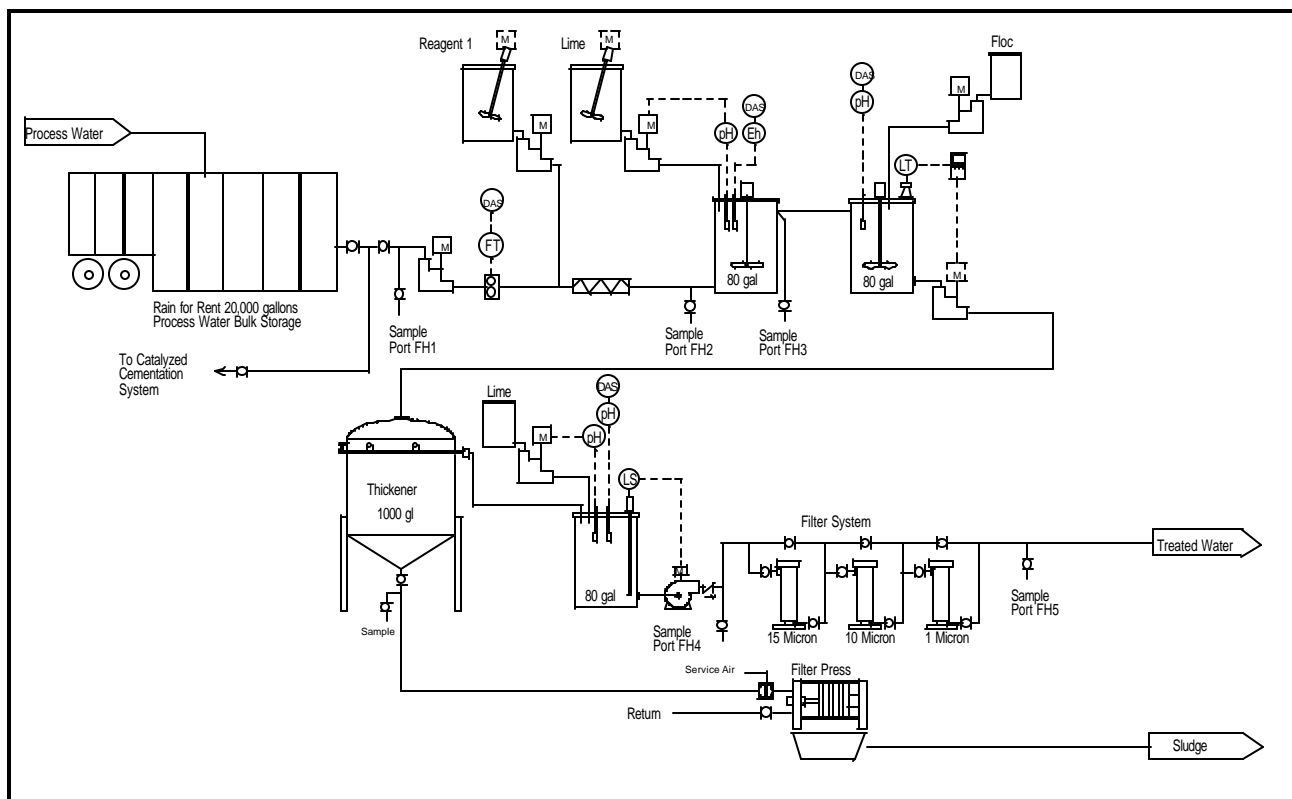
#### *Catalyzed Cementation of Selenium*

Catalyzed cementation has been developed to remove arsenic and other heavy metals such as thallium and selenium from water. The term catalyzed cementation describes the process's ability to remove contaminants from solution by cementation (adsorption) onto the iron surface. It is anticipated that the catalyzed cementation process will have the ability to treat and remove selenium from solution regardless of its valence state (+6 or +4). To optimize the cementation process, proprietary catalysts are added to increase the removal efficiency of the process. This process has been shown in similar tests to reduce selenium concentrations below the Maximum Contaminant Level of 50 ppb. The ferrihydrite precipitation process and the catalyzed cementation process are shown together in Figure 21. (The catalyzed cementation process is shown in the lower half of the drawing.)

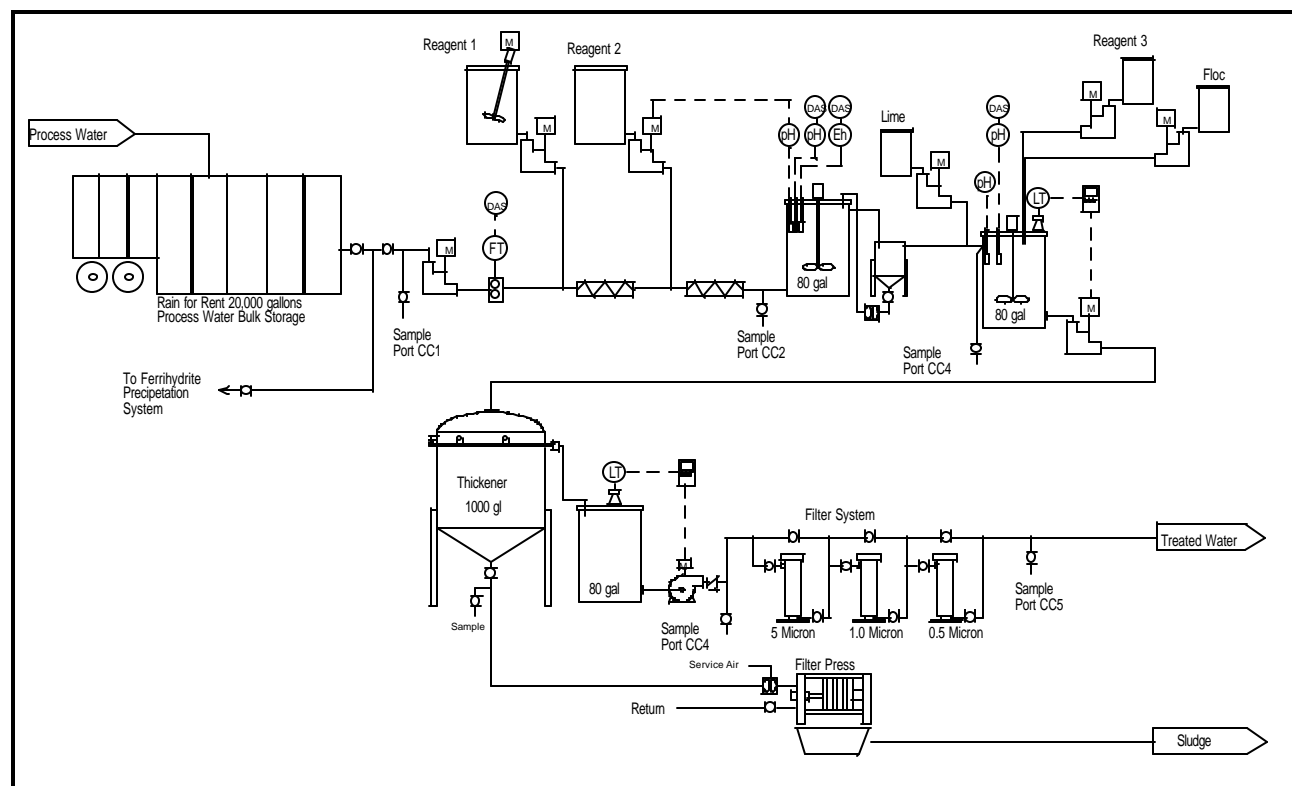
#### *Biological Reduction of Selenium*

To accomplish biological selenium reduction, researchers at Applied Biosciences of Park City, Utah, have developed a process using baffled anaerobic solids bed reactors (BASBRs). The process is depicted in Figure 22. Selenium (selenate and selenite) will be reduced to elemental selenium by specially developed biofilms containing specific proprietary microorganisms. This produces a fine precipitate of elemental selenium. The marketability of the elemental selenium product will be investigated during this project. This process is being demonstrated using equipment designed and constructed by ABC with assistance from Kennecott Utah Copper Corporation.

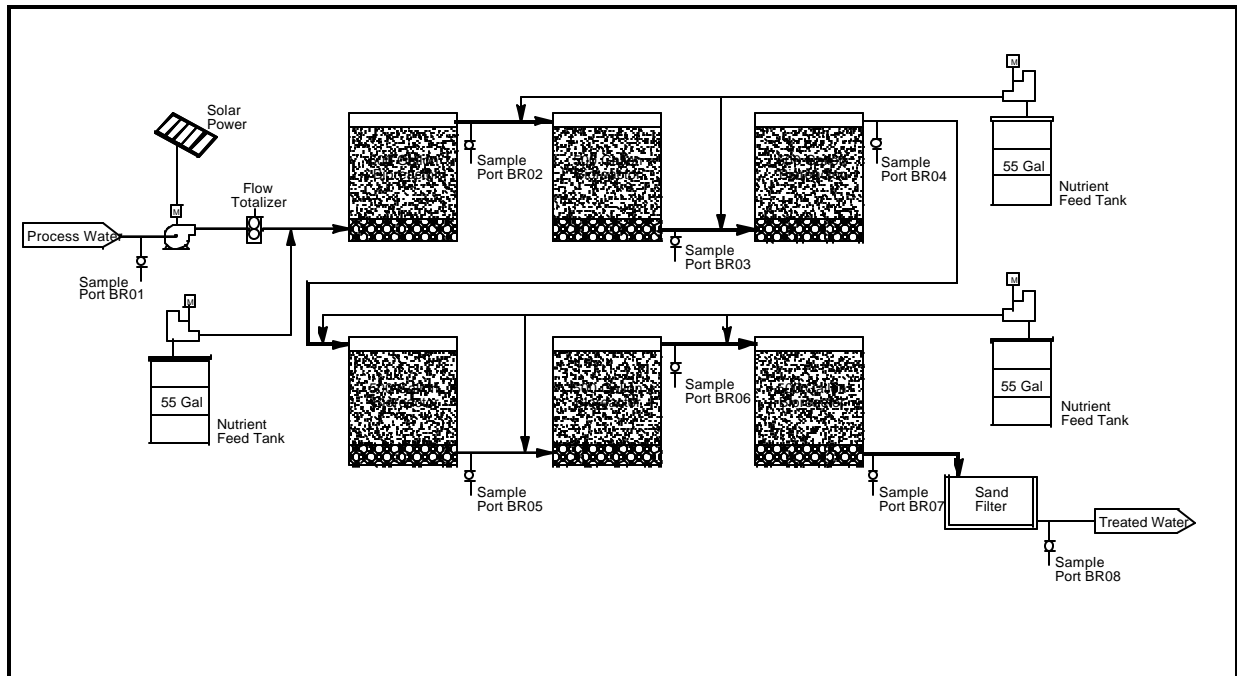
The pilot-scale BASBRs will be used to investigate the feasibility of using a defined mixture of *Pseudomonas* and other microbes for removing selenium from influent water.



**Figure 21a. Ferrihydrite precipitation process flow diagram.**



**Figure 21b. Catalyzed cementation process flow diagram.**



**Figure 22. Biological selenium reduction process flow diagram .**

## Status

Bench-scale optimization works for all three technologies and is complete. The project-specific Quality Assurance Project Plan is being finalized. The field demonstration of the selected selenium removal technologies is scheduled for late October 1999.

## ACTIVITY III, PROJECT 21: INTEGRATED PROCESS FOR TREATMENT OF BERKELEY PIT WATER

### Project Overview

The objective of this project is to develop integrated, optimized treatment systems for processing Berkeley Pit water. The Berkeley Pit is

an inactive open-pit copper mine located in Butte, Montana. Currently containing approximately 30 billion gallons of acidic, metals-laden water, the Berkeley Pit is filling at a rate of approximately 3 million gallons per day and is a good example of acid rock drainage.

Two optimized flowsheets will be developed for this project. One flowsheet is to be oriented toward minimizing the overall cost of water treatment to meet discharge requirements— this will include not only water treatment equipment but also sludge handling/ management. The other flowsheet is to be oriented toward also meeting discharge requirements but includes the recovery of products from the water (copper, metal sulfates, etc.) to potentially offset treatment costs and result in overall better economics.

### Technology Description

The project will evaluate proven technologies as well as technologies with credible pilot-scale

supporting data. Technologies with only laboratory testing history will not be included, which would include technologies for sludge management, solid/liquid separation, dewatering, drying, etc., as well as technologies for product recovery from water. The goal is to assemble the sequence of unit operations resulting in the most attractive overall economics.

## Status

The project work plan was completed. An effort to gather information and costs for sludge handling/dewatering equipment was initiated. Reference flowsheets for the two flowsheet development scenarios were identified, and technical/economic verification efforts were initiated. A conceptual design for a sludge repository was initiated; this was significant since the repository location had only recently been designated, which would allow reasonable cost estimates to be performed for the first time. Berkeley Pit stakeholders were contacted for input on the project.

## **ACTIVITY III, PROJECT 23: REVEGETATION OF MINING WASTE USING ORGANIC SOIL AMENDMENTS AND EVALUATE THE POTENTIAL FOR CREATING ATTRACTIVE NUISANCES FOR WILDLIFE**

### Project Overview

The objective of this project is to develop technical information on using organic soil amendments to improve soil conditions, reduce erosion, enhance plant establishment, stabilize toxic metals, and reduce plant uptake of metals from mine waste to vegetation that could present a food chain risk for foraging wildlife. Thousands of abandoned mine and mineral processing sites throughout the United States are very unattractive and can be a significant environmental hazard. The federal government and responsible parties need to develop cost-effective remedial approaches to effectively manage these

large areas that are contaminated with a wide variety of metals. Natural revegetation is often prevented in these areas because of low pH, phytotoxic concentrations of metals, poor physical structure for plant growth, nutrient deficiencies, and slopes too steep for plant establishment. Mine waste reclamation research frequently includes the addition of organic soil amendments, since mine waste materials are typically subsurface in origin and have minimal organic content. However, the diversity of organic soil amendments used and the lack of uniformity within each category of material make comparisons among sites and studies difficult. In addition, while it is generally agreed that organic soil amendments are capable of stabilizing mine waste metals, the potential for post reclamation impacts to wildlife due to plant uptake of those metals requires further research.

## Technology Description

MSE is proposing to establish field plots at the Big River Mine Tailings Site and the Leadwood Chat Tailings Site in Missouri in the spring of 2000. The plots will be evaluated to determine vegetation establishment, biomass production, and plant uptake of metals. Procedures for establishing, maintaining, and evaluating the plots will be broadly applicable and reproducible so that subsequent studies at other locations will produce comparable information. Three organic soil amendments will be evaluated at three varying application rates. Plant species selection will be based on previous success at the sites. Because species screening is not one of the project objectives, the number of species planted will be limited. The project will be evaluated for three growing seasons.

## Status

This project was initiated at the end of FY99. A site visit to Missouri was conducted to select the plot areas that will be utilized for the demonstration. Also, samples were collected from the two selected sites for site characterization. A conceptual design was initiated. Field testing is planned to begin in the spring of 2000. Project completion is expected in December 2002.



## ACTIVITY IV OVERVIEW

The objective of this activity is to develop, qualify, and screen techniques that show promise for cost-effective remediation of mine waste. The most promising and innovative techniques will undergo bench- or pilot-scale evaluations and applicability studies to provide an important first step to full-scale field demonstrations. Each experiment is assigned as an approved project with specific goals, budget, schedule, and principal team members.

### ACTIVITY IV, PROJECT 8: PIT LAKE SYSTEM—CHARACTERIZATION AND REMEDIATION FOR THE BERKELEY PIT

#### Project Overview

An interdisciplinary team of Montana Tech researchers undertook a preliminary study of several aspects of the Berkeley Pit to gather specific information about that pit lake system and to gather information that could be generally applied to all pit lakes.

In this work, the chemical and biological characteristics of the water and sediments in the Berkeley pit were studied to provide water quality data that can be used to predict future water quality, to evaluate the potential for natural remediation by bacteria such as sulfate-reducers, and to determine if partial in situ remediation would be practical prior to the pump and treat technologies prescribed in the EPA Record of Decision.

To provide the water and sediment for the characterizations, the Montana Bureau of Mines and Geology sampled the water at two locations and at depths from the surface to the bottom (0 to 1200 feet) at set intervals. Sampling was also done in both the spring and the fall to account for climatic effects on surface water quality.

## Status

The water chemistry of the Berkeley Pit lake varies with the volume of water entering it from various sources and the changes in the seasons. The amount of metals precipitated from the surface water layer is dependant of the area of the water surface exposed to the air and the climatic changes associated with the four seasons. The chemistry of the deep water is relatively constant throughout the year.

Organic carbon, a food source for bacteria is present in the water. The concentration of organic carbon is relatively that of the natural occurring springs in the area of the Berkeley Pit.

No sulfate-reducing bacteria activity was detected in the water or the sediments. However, a number of fungi and yeasts were isolated, and these will be further studied.

The report for this study is complete. This work lead to the more specific research presented in Activity IV, Projects 9, 10, and 11.

### ACTIVITY IV, PROJECT 9: PIT LAKE SYSTEM—DEEP WATER SEDIMENT/PORE WATER CHARACTERIZATION AND INTERACTIONS

#### Project Overview

This project involves collecting samples and data to identify the sediment/pore water resident conditions, solution phase speciation, and solid phase chemical, physical, and mineralogical characteristics that presently exist within the upper layer and deeper layers of the sediment/pore water deep-water deposits.

The thesis to be proven (or disproven) by this investigation is that conditions are formed in the sediment system that allow for the formation of metal sulfides, i.e., reducing/pH conditions that support the formation of metal sulfides. If sulfide



presence in the sediment layer is shown, then the conditions will be favorable for long-term environmentally safe storage of metal-bearing compounds. Also, if strong reducing conditions exist in the sediment layer, then pore water is anticipated to be relatively clean (compared to upper layer water). Therefore, assuming our thesis is proven, several remediation techniques can be envisioned, e.g., metal sulfides could be formed from dissolved metals in the upper water system (which settle to the sediment deposit) by sulfide addition (or by sulfate-reducing bacteria) or a portion of the pit water could be treated externally by sulfide addition (or by sulfate-reducing bacteria) and the resulting sludge pumped into the sediment layer for safe storage; or relatively clean water could be pumped from the sediment region that would require only a polishing type final cleanup before release.

The specific tasks to be undertaken during this study include:

- Collecting deep water upper layer sediment samples.
- Collecting subsurface sediment/pore water samples.
- Characterizing and speciation of sediment solids and subsurface pore water.
- Modeling the system to understand the controlling sediment formation mechanism (this includes sediment formation experimentation).

## Status

The project was completed in December 1998, and the final report was published.

## ACTIVITY IV, PROJECT 10: PIT LAKE SYSTEM—BIOLOGICAL SURVEY OF BERKELEY PIT WATER

### Project Overview

Very little is known about the organisms that are found in Montana's waters impacted by acid mine waste. One of the few references to algae is simply a checklist without illustrations; however, little mention is made of mine areas. The only other person who has studied the algae (mostly diatoms) of Montana is Loren Bahls, but much of his work is unpublished (personal communication). Even less is known about the diversity of protists, fungi, and bacteria that inhabit these sites. Consequently, this area of research is quite intriguing because numerous organisms are clearly growing in water as low as pH 2 loaded with high accumulations of metals. What is most significant is that these extremophiles may be potential organisms to bioremediate contaminated sites.

The Berkeley Pit Lake system is one of the largest contaminated sites in North America and is part of the largest superfund site in the United States. The Pit is 542 m deep with a lateral extent of approximately 1.8 km by 1.4 km across the rim. The only larger pit mine in the United States is the Bingham Pit in Salt Lake City, Utah. The chief difference between the two pits is that the Berkeley Pit has approximately 266 m of water in it that is rising at a rate of about 8 m/year. Consequently, this represents roughly 1,140 billion liters of pH 2.7, metal laden, contaminated water and has been designated a Superfund project for clean-up. This emphasizes how important this research may be to the State of Montana and to the United States, but there are even more contaminated, larger sites throughout the world. It is the goal of this research to begin to gain an understanding of the microbial ecology of the Berkeley Pit Lake system, which will ultimately provide necessary data for bioremediation studies and may apply to other contaminated locales worldwide.

The primary goals of this study are both to determine species diversity and numbers for organisms present in these mine waste areas and to determine their potential ecological role in the system for bioremediation. Various beneficial processes occur because of algal and photosynthetic bacterial growth in aquatic habitats. These processes are important because they may affect the chemistry in a number of ways.

- These organisms are primary producers and, as a result of their physiology, naturally produce bicarbonate to raise the pH of acidic solutions in which they are growing.
- As algae grow, they leak excess photosynthates that, in turn, promote bacterial growth.
- These microbes play a role in the biological magnification of toxic materials (each trophic level of the food web will increase the concentration of many metals ten times).
- Photoautotrophs oxygenate the water that will promote aerobic activity.
- Photoautotrophs are important in biogeochemical cycling of carbon, nitrogen, phosphorus, sulfur, and other elements—most importantly nitrogen fixation and sulfate reduction.
- Algal cells may directly sorb metal ions through several mechanisms that include ion exchange, complexation, and physisorption.
- Accumulation and eventual decomposition of algal biomass will increase the organic carbon component of the mine waste systems which, in turn, will promote heterotrophic growth of bacteria, fungi, and protozoans.
- Algal biotransformation or enzyme-catalyzed conversion of metals will result in less toxic organic compounds.

## Status

The project was completed in December 1998, and the final report was published.

## ACTIVITY IV, PROJECT 11: PIT LAKE SYSTEM CHARACTERIZATION AND REMEDIATION FOR BERKELEY PIT—PHASE II

### Project Overview

An interdisciplinary team of Montana Tech researchers is currently studying several aspects of the Berkeley Pit Lake system to better understand the system as a whole, which may lead to new or improved remediation technologies to be used during future cleanup. The information obtained from the studies will be used to predict future qualities of the water, to evaluate the natural rate of remediation, to determine if partial in situ remediation may be practical prior to expensive pump and treat remediation, and to predict water quality for similar bodies of water in the United States. The following research is being conducted on the Berkeley Pitlake: Organic Carbon in the Pit Lake Sediments; Water/Wall Rock Interactions; Bioremediation of the Berkeley Pit Lake System; and Tailings Deposition into the Berkeley Pit

### *Organic Carbon in Berkeley Pit Sediments*

Late in 1997, the Mine Waste Technology Program funded several projects to chemically and physically characterize the Berkeley Pit Lake water as a function of depth at several positions within the pit. Reports on this work are in preparation for the Berkeley Pit Characterization Project, Mine Waste Technology Program Activity IV, Project 8. The section, *Analyzing Organic Substances in the Berkeley Pit Water*, has demonstrated that the organic carbon content of the water is approximately 2 to 3 ppm. There appears to be some minor changes in total organic carbon (TOC) concentration as a function of depth in the pit lake.

Considering the sources of water for the pit lake and the similar concentrations of TOC in the in-flow and pit lake waters, it is reasonable to assume that the organic material in the water of the Berkeley Pit Lake is typical of alpine ground and surface waters. Although not yet identified directly, it is also

reasonable to assume that a major fraction of the TOC is humic material. Humic substances are well known to be important factors in controlling the chemistry of aquatic ecosystems. Humic material bind hydrogen ions, metal ions, and other organic compounds; adsorb strongly at aqueous/solid interfaces; and participate in the redox and photochemistry of surface waters.

### ***Wall Rock/Water Interactions***

To understand the processes of water-rock interaction in the pit environment, we need to know more about the mineralogy of the pit walls and how these minerals interact with rain water, oxidized (shallow) pit water, and reduced (deep) pit water. The main objectives of this project will be: 1) to collect a suite of samples from the north high wall of the Berkeley pit, focusing on material that contains abundant secondary minerals (post mining oxidation products); 2) to collect a suite of samples from the walls of the Lexington tunnel (e.g., dripstones forming at acid rock drainage seeps); 3) to characterize the mineralogy of these samples by the scanning electron microscopy/energy dispersive spectrometer and x-ray diffraction; and 4) to interact selected samples with distilled water, oxidized pit water, and reduced pit water to document changes in solution chemistry (e.g., pH, metal concentration) and solid mineralogy with time.

### ***Bioremediation of the Berkeley Pit Lake System***

Very little is known about the organisms that are impacted by mine waste in the Berkeley Pit Lake system. It is known that if heterotrophic and autotrophic organisms are properly nurtured, they can bioremediate mine waste-influenced areas as a benefit of their physiological processes. However, before any type of bioremediation of an ecosystem can begin, it is essential to gain a fundamental understanding of the components of the microbial community. Defining the baseline community structure is the first step toward understanding the interaction of the different biota and toward assessing any improvement in biodiversity within the biotic community. Progress toward this understanding has been made clearer by previous research.

### ***Tailings Deposition into Berkeley Pit***

One potential course of action of Montana Resources in the near future is to deposit their tailings into the Berkeley Pit instead of pumping them up to the Yankee Doodle Tailings Pond. As a result, a high pH tailings slurry would be mixed with the low pH Berkeley Pit water. The exact results tailings deposition into the Berkeley Pit is not clear. This research will focus on three main areas: 1) water quality of Berkeley Pit water as tailings are deposited; 2) long-term stability of tailings/water mixture; and 3) long-term stability of tailings alone.

### **Status**

This project is under way and is scheduled to be completed by February 2000.

## **ACTIVITY V OVERVIEW TECHNOLOGY TRANSFER**

This activity consists of making technical information developed during Mine Waste Technology Program (MWTP) activities available to industry, academia, and Government agencies. Tasks include preparing and distributing MWTP reports, presenting information about MWTP to various groups, holding Interagency Agreement Management Committee meetings, sponsoring mine waste conferences, and working to commercialize treatment technologies.

### ***Fiscal Year Highlights***

- The FY99 MWTP Annual Report was published summarizing fiscal year accomplishments. A similar report will be published each year.
- Several MWTP professionals appeared at varied meetings to discuss the Program with interested parties. Many mine waste conferences, as well as mining industry meetings, were attended.
- Investigations were conducted on how best to integrate and interface with the ongoing technology transfer activities of the Federal Government.

## ACTIVITY VI OVERVIEW TRAINING AND EDUCATION

Through its education and training programs, MWTP continues to educate professionals and the general public about the latest information regarding mine and mineral waste cleanup methods and research.

As a result of rapid technology and regulatory changes, professionals working in the mine- and mineral-waste areas often encounter difficulties in upgrading their knowledge and skills in these fields. In recent years, the environmental issues related to the mining and mineral industries have received widespread public, industry, and political attention. While knowledge of current research and technology is vital for dealing with mine and mineral wastes, time and costs may prevent companies from sending employees back to the college classroom.

Through short courses, workshops, conferences, and video outreach, Activity VI of the MWTP educates professionals and the general public and brings the specific information being generated by bench-scale research and pilot-scale technologies to those who work in mine- and mineral-waste remediation.

### ***Fiscal Year 1999 Highlights***

- The *Mine Design, Operations, and Closure Conference '99*, conducted in April 1999, continued last year's interagency cooperation. The 5-day event was cosponsored by the U.S. Forest Service; U.S. Bureau of Land Management; Montana Department of State Lands; MSE; Haskell Environmental Research Studies Center; several other private companies; and Montana Tech. During the conference, experts presented overviews on such topics as predictive chemical modeling for acid mine drainage, mine water quality source control, state-of-the-art containment technologies, and innovative pit reclamation. Over 130 mine operators, consultants, and professionals from the private and public sectors attended the conference.

- The Mine and Mineral Waste Emphasis Program has an enrollment of 11 students with all of them receiving funding from MWTP. This is an interdisciplinary graduate program that allows students to major in their choice of a wide variety of technical disciplines while maintaining an emphasis in mining and mineral waste.
- A group of Mine and Mineral Waste Emphasis graduate students attended the Mine Design, Operations, and Closure Conference '99.
- A cooperative agreement is in place for work with the Haskell Environmental Research Studies Center at Haskell Indian Nations University.
- Graduate students in the Mine and Mineral Waste Emphasis Program are working on projects in Activities III and IV.
- As part of the Native American Initiative, Montana Tech presented three short courses: Mining and the Environment at Fort Belknap, and Acid Rock Drainage at both Fort Belknap and Salish Kootenai College. Also, Montana Tech is planning on presenting three more short courses next year. An environmental learning community is being set up to house the short courses and Web courses to make them accessible to Native American communities around the country.

### ***Future Activities***

The following training and educational activities are scheduled for the first part of 2000:

- MWTP Training and Educational activities will offer the Mine Design, Operations, and Closure Conference 2000 in April 2000.
- MWTP is working on a cooperative education package for the Montana Department of Environmental Quality.
- All funded Mine and Mineral Waste Emphasis Program graduate students will work on mine waste-oriented projects as a part of their funding requirements.

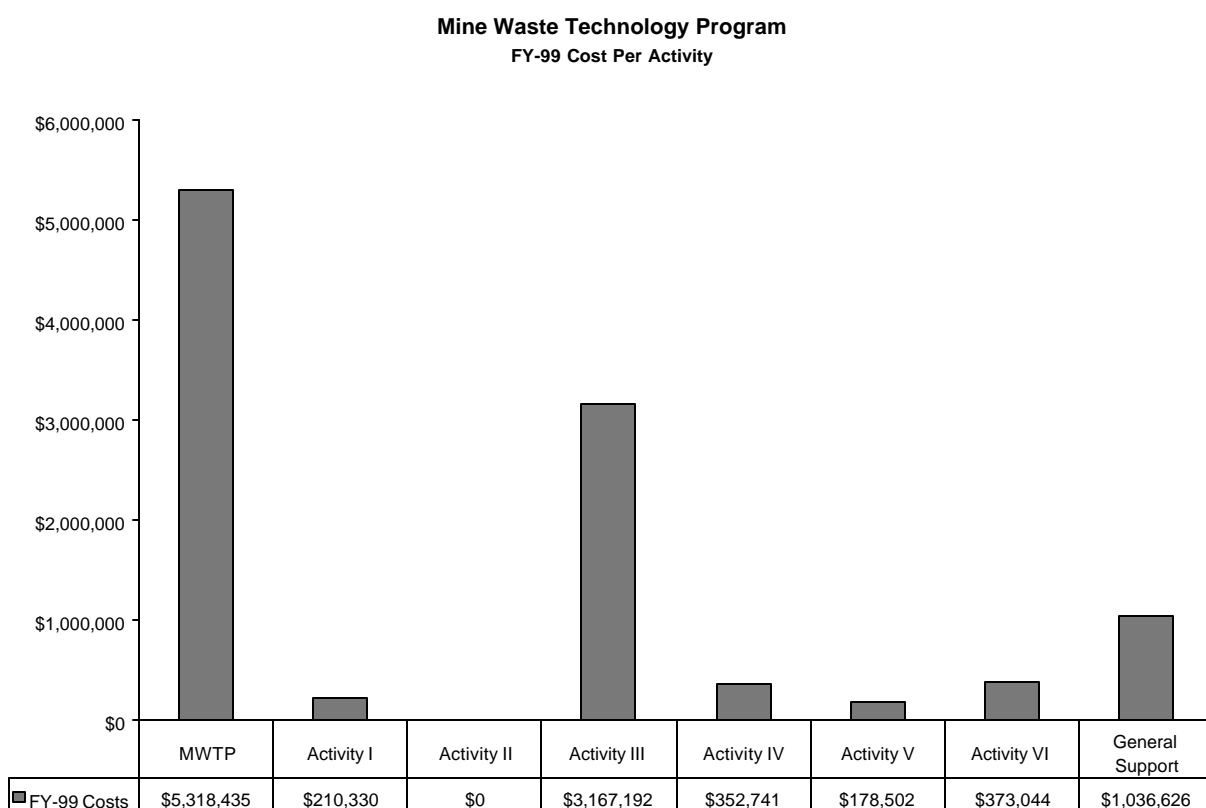


# FINANCIAL SUMMARY

Total expenditures during the period October 1, 1998, through September 30, 1999, were \$4,850,374, including both labor and nonlabor expense categories.

Individual activity accounts are depicted on the performance graph in Figure 23.

The cumulative authorized budget for the period was \$6,477,136.



**Figure 23. Mine Waste Technology Program FY99 performance graph, costs per activity.**



# COMPLETED ACTIVITIES

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## ACTIVITY III, PROJECT 1: REMOTE MINE SITE DEMONSTRATION

### Project Overview

Acidic metal-laden water draining from remote, abandoned mines has been identified by the EPA as a significant environmental hazard to surface water in the Western United States. In Montana alone, more than 3,000 such sites have been identified, and wastes from these mines have damaged over 1,100 miles of surface water in the State.

The EPA asked MSE to develop a treatment facility at one of these sites to treat acidic metal-laden water. Due to the remote nature of these locations, this facility was required to operate for extended periods of time on water power alone, without operator assistance.

An example of a remote mine site with a point-source aqueous discharge is the Crystal Mine. Located 7 miles north of Basin, Montana, the Crystal Mine was an ideal site for this demonstration. In addition, the site had been identified by the Montana State Water Quality Bureau as a significant contributor of both acid and metal pollution to Uncle Sam Creek, Cataract Creek, and the Boulder River. This project demonstrated a method for alleviating nation-wide environmental problems associated with remote mine sites.

### Technology Description

The Crystal Mine demonstration treated a flow of water ranging from 10 to 25 gallons per minute, approximately half of the total mine discharge. The process consisted of the following six unit operations:

- Initial Oxidation—atmospheric oxygen partially oxidizes ferrous iron to the ferric form.
- Alkaline Addition—reagents form metal hydroxide solids.
- Secondary Oxidation—atmospheric oxygen oxidizes additional ferrous iron to the ferric form.
- Initial Solid/Liquid Separation—settling ponds trap precipitated solids.
- pH Adjustment—atmospheric carbon dioxide lowers the pH.
- Secondary Solid/Liquid Separation—settling pond retains additional precipitated solids.

### Results

The Remote Mine Site Demonstration Project at the Crystal Mine was conducted in the field for 2 years under all weather conditions. Construction of buildings, ponds, and associated mine site infrastructure began in late May 1994 and was completed in early August 1994. Acid mine drainage from the lower portal of the Crystal Mine began passing through the system on a full-time basis in early September 1994. Analytical data from the project showed a greater than 75% removal of toxic metals from the mine drainage. The project was closed out, and the final report was issued.



## **ACTIVITY III, PROJECT 2: CLAY-BASED GROUTING DEMONSTRATION**

### **Project Overview**

Surface and groundwater inflow into underground mine workings becomes a significant environmental problem when water contacts sulfide ores, forming acid drainage. Clay-based grouting, the technology selected for this demonstration, has the ability to reduce or eliminate water inflow into mine workings by establishing an impervious clay curtain in the formation.

### **Technology Description**

Groundwater flow is the movement of water through fissures and cracks or intergranular spaces in the earth. With proper application, grout can inhibit or eliminate this flow.

Grouting is accomplished by injecting fine-grained slurries or solutions into underground pathways where they form a groundwater barrier. The Ukrainian clay-based grouting technology was selected for testing and evaluation because it offered a potentially long-term solution to acid mine drainage problems.

Clay-based grouts are visco-plastic systems primarily comprised of structure-forming cement and clay-mineral mortar. When compared to cement-based grouts, clay-based grouts offer the following advantages: better rheological characteristics, greater retention of plasticity through the stabilization period, and less deterioration during small rock movement.

### **Results**

The Mike Horse Mine near Lincoln, Montana, was the project site. A major factor in the site selection was an identified point-source flow from Mike Horse Creek into the mine causing acid drainage that could potentially be controlled using grouting technology.

Approximately 1,600 cubic yards of clay-based grout were injected into the fracture system adjacent to the Mike Horse Mine. The grout was pumped into boreholes using packers to ensure the proper placement of grout at selected intervals. Grout injection was initiated September 1994 and completed in November 1994. A second phase of grout injection was planned for the summer of 1995; however, high water dammed up within the mine caused extensive damage to the mine and to the monitoring stations used for the demonstration. As a result, Phase Two was discontinued.

From the minimal amount of monitoring data that was collected, it was determined that the total discharge from the mine was reduced by approximately 30%.

## **ACTIVITY III, PROJECT 4: NITRATE REMOVAL DEMONSTRATION**

### **Project Overview**

The presence of nitrates in water can have detrimental effects on human health and the environment. Nitrates may be present in mine discharge water as a result of mining or other industrial activities.

To comply with federal and state water quality standards, mining companies have typically used ion exchange or reverse osmosis to remove nitrates from discharge water. However, both are expensive and generate a concentrated nitrate wastestream requiring disposal.

### **Technology Description**

Mine Waste Technology Program (MWTP) personnel undertook an extensive search to evaluate innovative nitrate removal technologies. Of the twenty technologies screened, the following three showed the most promise in making nitrate removal more cost effective and environmentally responsible:

- ion exchange with nitrate-selective resin;
- biological denitrification; and
- electrochemical ion exchange (EIX).

MWTP personnel believed the best solution to the nitrate problem was some combination of the three technologies that balanced capital costs with operating costs, reliability, and minimization of wastestreams requiring disposal. Each combination had advantages and disadvantages that were addressed during the project.

## Results

The Nitrate Removal Demonstration Project was conducted at the TVX Mineral Hill Mine near Gardiner, Montana. Conventional ion exchange was used to remove nitrate from the mine water and produce a concentrated brine for additional testing. Biological denitrification units and an EIX unit were used to process both mine water and concentrated nitrate brine.

The goals of the project were to remove nitrate to less than 10 milligrams per liter (mg/L) of nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) in the effluent and to minimize the amount of waste produced. Of all the technology combinations tested, biological denitrification of concentrated nitrate brine was the most successful at meeting these goals.

The nitrate ion exchange (NIX) unit was produced by Altair, Inc. As expected, the NIX unit worked well and removed nitrate from the mine water very effectively. Input levels of 20 to 40 mg/L  $\text{NO}_3\text{-N}$  were typically reduced to less than 1 mg/L. The unit also produced a concentrated brine with high levels of nitrate and chloride. Frequent equipment shutdowns and muddy mine water did not affect the operation of the NIX unit.

Biological denitrification was performed on both mine water and concentrated brine. This process worked well to eliminate nitrate in brine. Except for two process upsets, nitrate was removed to levels less than 10 mg/L  $\text{NO}_3\text{-N}$ . This removal rate met the project goals and was typically greater than 99%.

Biological denitrification of the raw mine water was less successful. A removal rate of approximately 50% was typically achieved. This data was taken from an operating denitrification reactor at the mine. Past data had shown that this reactor was very effective at nitrate removal. Apparently, the frequent shutdowns and startups had a detrimental effect on these reactors.

The electrochemical ion exchange unit was built by Selentec, Inc. Electrochemical ion exchange was unsuccessful at removing much nitrate from the concentrated brine because of the presence of high concentrations of a competing anion—chloride.

Electrochemical ion exchange was able to remove nitrate from the raw mine water more effectively than from the brine. Nitrate was removed at first; however, fouling of the resin by dirty water occurred quickly, and the process was rendered ineffective after one batch. Filters were installed, but the nature of the particles made filtration difficult.

## ACTIVITY III, PROJECT 5: BIOCYANIDE DEMONSTRATION

### Project Overview

The primary use of cyanide in the mining industry is to extract precious metals from ores. The use of cyanide has expanded in recent years due to increased recovery of gold using heap leach technologies. Cyanide can be an acute poison and can form strong complexes with several metals, resulting in increased mobility of those metals. As such, cyanide in mine wastewater can contribute to environmental problems.

These potential problems have led to the development of several methods to destroy cyanide and cyanide complexes in mining wastewater. Most of these processes use chemicals to oxidize the cyanide and produce nontoxic levels of carbon dioxide and nitrogen compounds, which are relatively expensive to operate.

## Technology Description

Biological destruction of cyanide compounds is a natural process that occurs in soils and dilute solutions. To take advantage of this natural destruction, a strain of bacteria was isolated by researchers at Pintail Systems, Inc. This bacteria has been tested on cyanide-contaminated mine waters and has shown degradation rates of over 50% in 15 minutes.

The main goal of this project was to use a strain of bacteria to destroy cyanide associated with precious metal mining operations. Another project goal was to develop a reactor design that would best use the cyanide-degrading effects of the bacteria to destroy cyanide from mining wastewater.

The field demonstration portion of the project was located at the Echo Bay McCoy/Cove Mine, southwest of Battle Mountain, Nevada. The mining rate at the mine exceeds 160,000 tons of ore per day. Milling of high-grade and sulfide ores occurs simultaneously with the cyanide solution heap leaching of lower grade ores. These cyanide solutions contain 500 to 600 mg/L of weak acid dissociable (WAD) cyanide with other contaminants, such as arsenic, copper, mercury, selenium, silver, zinc, and nitrate.

## Results

In FY96, a field-scale unit was constructed at the McCoy/Cove Mine to degrade cyanide in an existing process stream. The unit was designed to reduce the WAD cyanide concentration from 500 mg/L to less than 0.2 mg/L at flow rates of approximately 1 gallon per minute.

A bioaugmentation phase was initiated to isolate organisms and select the ones that degrade cyanide most effectively. To initiate the project, Pintail Systems, Inc., collected water samples from the mine site to isolate indigenous organisms capable of effectively degrading cyanide and performed bioaugmentation studies at their Colorado laboratory. During the bioaugmentation phase, the bacteria were subjected to increasing concentrations of cyanide to select the most capable organisms.

The bacteria selected during the bioaugmentation process were then placed on fixed growth media in bench-scale reactors. Next, actual cyanide mine water was processed through the reactors to study the kinetics of cyanide degradation. The results from these tests were then used to design the pilot-scale reactors to be used at the mine. The process train consisted of tanks where the aerobic and anaerobic bacteria were grown in large quantities. The bacteria were then pumped to the reactors for reinoculation. The cyanide solution entered the aerobic reactor first where aerobic organisms degraded a large portion of the cyanide. The solution then moved through a series of anaerobic units for further degradation. Finally, an aerobic polishing step removed the last traces. Since cyanide is known to degrade by mechanisms other than biological, a series of control reactors was installed to run concurrently with the biological reactors.

Testing of the pilot-scale unit was performed during the summer of 1997. Cyanide and heavy metals were substantially removed from the mine process water. The pH was consistently neutralized. A preliminary scale-up cost estimate indicated substantial savings over conventional technologies. The final report was delivered to EPA in FY98.

## ACTIVITY III, PROJECT 6: POLLUTANT MAGNET

### Project Overview

This project was forwarded to the Mine Waste Technology Program (MWTP) by personnel from EPA's National Risk Management Research Laboratory. The concept of the pollutant magnet was to develop, produce, and test particles that have specific magnetic properties and have the ability to remove specific pollutants from a wastestream. After program personnel reviewed the project, it was dropped from MWTP due to its similarity with competing technologies that were more developed and had a nonmining specific use.

## ACTIVITY III, PROJECT 7: ARSENIC OXIDATION

### Project Overview

The Arsenic Oxidation Project was proposed to demonstrate and evaluate arsenic oxidation and removal technologies. The technology being demonstrated during this project was developed jointly by the Cooperative Research Center for Waste Management and Pollution Control Limited and the Australian Nuclear Science & Technology Organization (ANSTO) from Lucas Heights Research Laboratories in Lucas Heights, New South Wales, Australia.

Arsenic contamination in water is often a by-product of mining and the extraction of metals such as copper, gold, lead, zinc, silver, and nickel. This contamination will continue to grow as high-grade ores with low arsenic content are being depleted and the processing of sulphide ores with high arsenic content becomes increasingly common. In most cases, it is not economical to recover the arsenic contained in process streams because there is little demand worldwide for arsenic. Arsenic can be present in leachates from piles of coal fly ash, in contaminated groundwaters, in geothermal waters, and in acid drainage from pyritic heaps resulting from the past practices of mining metallic ores.

Trivalent arsenic, arsenic(III), or arsenite compounds have been reported to be more toxic than the corresponding pentavalent arsenic, arsenic(V) or arsenate forms, and much more difficult to remove from solution. Consequently, there is a need to convert arsenic(III) to arsenic(V) to achieve effective arsenic removal from solution.

### Technology Description

The small-scale pilot project demonstrated a two-step process for removing arsenic from contaminated mine water. The first step and primary objective of this project was to evaluate the effectiveness of a photochemical oxidation process to convert dissolved arsenic(III) to arsenic(V) using dissolved oxygen as the oxidant.

The technology provides a method for the oxidation of arsenic(III) in solution by supplying an oxidant, such as air or oxygen, and a nontoxic photo-absorber, which is capable of absorbing photons and increasing the rate of arsenic(III) oxidation to the solution. The photo-absorber used is economical and readily available. Ultraviolet oxidation using high-pressure mercury lamps and solar energy was tested. The second step of this project resulted in the removal of arsenic(V) from the solution by using an accepted EPA method, adsorption using ferric iron.

### Results

The field demonstration and final report were completed. The photochemical oxidation process was very effective at oxidizing arsenite to arsenate at optimum conditions in the batch mode for both the solar tests and the photoreactor tests; however, design problems with the photoreactor unit in the continuous mode would not allow ANSTO to achieve their claim of 90% oxidation of arsenite in solution. Channeling of the process waters in the photoreactor unit was the reason for poor oxidation of arsenite, and steps to correct the problem during the field demonstration were unsuccessful. Modifications to the baffle system are necessary to prevent further channeling.

## ACTIVITY III, PROJECT 9: ARSENIC REMOVAL

### Project Overview

The purpose of the Arsenic Removal Project was to demonstrate the effectiveness of two innovative technologies and the best demonstrated available technology (BDAT) to remove arsenic from mineral industry effluents to below 50 parts per billion (ppb). Table AIII, P9-1 shows the removal and economic analysis of these tests. Two of the treated effluent streams were from the ASARCO East Helena lead smelter; the scrubber blowdown water contained > 3 grams per liter arsenic and other associated metals, and the water treatment thickener overflow water contained approximately

6 parts per million arsenic. A third stream from the TVX Mineral Hill Mine 1,300-foot portal groundwater contained approximately 500 ppb arsenic.

**Table AIII, P9-1. Removal and economic analysis for Activity III, Project 9.**

Technology	Scrubber Blowdown (> 3 g/l As)	Thickener Overflow (~ 6 ppm)	Portal Groundwater (~ 500 ppb)	Cost/1000 gallons*
Mineral-Like Precipitation	< 10 ppb	< 10 ppb	< 10 ppb	\$0.30
Alumina Adsorption	—	200 ppb	21 ppb	\$0.70
Ferrihydrite Adsorption	—	< 50 ppb	< 50 ppb	\$0.55

\*Cost analysis is based on treating 300 gpm of groundwater containing 500 ppb arsenic. The accuracy of the measurement is +/-30%.

## Technology Description

### Mineral-Like Precipitation

The concept of this process is to strip arsenic (as arsenate) from solutions in a manner to produce mineral-like precipitated salts. The concept is to substitute arsenate into an apatite structure, thereby, forming a solid solution compound that would be thermodynamically stable in an outdoor storage environment.

### Alumina Adsorption

In this technology, arsenic is removed from solution by adsorbing it onto the surface of aluminum oxide over a specific pH range. After absorption, reagents are added to the alumina to desorb the arsenic into a concentrated brine. The concentrated arsenic brine solution is then treated using an iron adsorption technology to remove and stabilize the arsenic. The activated alumina in the process is recycled following the desorption process by treatment with sodium hydroxide.

### Ferrihydrite Adsorption

Ferrihydrite technology is the BDAT. For ferrihydrite adsorption to occur, ferric iron ( $\text{Fe}^{+3}$ ) must be present in the water. Dissolved arsenic is removed by a lime neutralization process in the presence of the ferric iron, which results in the formation of arsenic-bearing hydrous ferric oxide (ferrihydrite).

## Results

All three addressed technologies (iron coprecipitation, alumina adsorption, and mineral-like precipitation) showed favorable results for arsenic removal using groundwater; however, using industrial process wastewater, only two of the technologies (mineral-like precipitation and ferrihydrite adsorption) were capable of removing arsenic to below discharge standards. The complex chemistry of the industrial wastewater had a profound effect on arsenic removal using alumina adsorption.

## ACTIVITY IV, PROJECT 1: BERKELEY PIT WATER TREATMENT

### Project Overview

Bench-scale research on treating water from the Berkeley Pit was performed at Montana Tech of the University of Montana, in Butte, Montana.

The Berkeley Pit is an abandoned open-pit copper mine in Butte that has been filling with acidic water since pump dewatering of adjacent underground mines ceased in 1982. Flow into the Berkeley Pit has varied from approximately 7.5 million gallons per day initially to a current rate of approximately 2.5 million gallons per day.

The water in the Berkeley Pit was chosen for this project due to its accessibility, abundance, and the chemical similarities between it and other acidic mine waters. Studies had been conducted since 1986 on the Berkeley Pit water, and substantial analytical data had been developed, providing a foundation for this project.

### Technology Description

This project addressed treatability of the acid mine water that is accumulating in the Berkeley Pit. Appropriate treatment techniques were identified and developed. The overall goal was to evaluate technologies that produce clean water, allow for

safe waste disposal, and recover selected metals for resale. Technologies were evaluated by considering their effectiveness, technical feasibility, and potential for technology transfer to similar sites.

Experimental testing consisted of four major phases:

Physical oxidation, neutralization, and metal removal—this phase consisted of using alkaline reagents such as lime, limestone, or soda ash to neutralize the water and cause metals to precipitate as hydroxides. During neutralization, the water is aerated to oxidize iron(II) to iron(III), thereby enhancing sludge settling characteristics and promoting adsorption reactions. Metals removal efficiency and reaction kinetics were studied.

Metals separation and recovery—this phase is a two-stage hydroxide precipitation process. Sulfide and hydroxide precipitation were combined for more complete removal of metals. In other tests, metal sulfides were precipitated first to recover metal value, and scrap iron was used to cement copper before neutralization.

Use of milling waste—this phase consists of adding tailings slurry (primarily silicates, clay, lime, and limestone) directly to the Berkeley Pit water. This partially neutralized the water and removed some of the heavy metals. This in situ neutralization could potentially reduce reagent consumption and sludge formation for subsequent processing.

Diversion and treatment of various inflow water sources—this phase consists of investigating numerous water sources to determine the feasibility of diverting inflow water for treatment. Of the water that flows into the Berkeley Pit, one-third is surface water from the Horseshoe Bend area, and two-thirds is underground water that has penetrated through the mines and surrounding rocks.

## Results

All work for this project was completed, and the final report was published.

## ACTIVITY IV, PROJECT 2: SLUDGE STABILIZATION

### Project Overview

The Sludge Stabilization Project for mine waste was a bench-scale research project conducted at Montana Tech of the University of Montana.

The purpose of this research project was to study the properties and stability of sludges generated by remediation of acid mine waters. Results of the study were used to determine the best methods for sludge handling and disposal. One source of acid mine water being studied was from the Crystal Mine located approximately 7 miles north of Basin, Montana. The other source was the water from the Berkeley Pit in Butte, Montana. Besides being acidic, these waters contain toxic concentrations of iron, manganese, copper, zinc, arsenic, and sulfate, which is typical of many hard rock mining operations throughout the Western United States.

Past research on remediating acid mine water has focused primarily on water treatment techniques, and little emphasis has been placed on the stability of the sludge that is generated. To address this issue, faculty at Montana Tech, with expertise in chemistry, geochemistry, metallurgy, and environmental engineering, formed a research team to study the properties and stability of this sludge.

### Technology Description

The three types of sludge studied were: base-initiated sludge, inorganic sulfide-initiated sludge, and sulfate-reducing bacteria-initiated sludge. Appropriate solid-liquid separation techniques were used to isolate the solid phases for chemical characterization and stability tests.

Chemical characterization studies included quantifying the various element-solid associations, i.e., adsorbed, surface-precipitated, and coprecipitated contaminants. These studies then identified and quantified the divalent and trivalent

forms of iron and the trivalent, pentavalent, and methylated forms of arsenic. Once analytical techniques were verified for each of the sludges, they were applied to as-generated sludge and aged sludge.

Based on the chemical properties of these sludges, various storage environments were proposed and evaluated. The sludge stability research included standard regulatory tests and specifically designed tests, e.g., biostability tests, based on the selected specific disposal options, including storage in the natural environment. The results of these tests were translated into stability-enhancement studies, including the effect of aging the sludge in a temporary storage environment and treating the sludge with chemical additives before final storage.

The results of this sludge characterization and stability study identified characterization techniques and stability procedures that have application to sludges generated through other water-treatment procedures.

## Results

All work for this project was completed, and the final report was published.

## ACTIVITY IV, PROJECT 3: PHOTOASSISTED ELECTRON TRANSFER REACTIONS RESEARCH

### Project Overview

Research efforts under the Mine Waste Technology Program for the remediation of mine wastewaters have focused primarily on removing toxic heavy metal cations from solution. However, little attention has been given to toxic anions that can be associated with the heavy metal cations. Conventional treatment technologies generally require chemical process streams that generate

sludge by-products. Consequently, researchers at Montana Tech are attempting to identify and enhance naturally occurring processes that would help remediate toxic anions while minimizing treatment by-products. In this regard, the use of dissolved and solid photocatalysts is being investigated for removing cyanide and nitrate anions from mine wastewaters.

## Technology Description

On absorption of electromagnetic radiation (predominantly UV or visible light), photocatalysts enter an excited state where electrons are promoted from a valence band into a conduction band. Electrons in conduction bands can then be donated to species, causing that species to undergo reduction. Simultaneously, the absence of electrons in the valence band can cause other species to donate electrons to the valence band and thereby undergo oxidation. These electron-transfer reactions can cause the species to decompose. However, decomposition can only occur if the electrochemistry of the system is well defined, e.g., oxidation-reduction potential, pH, concentration, and temperature, and if the proper intensity and frequency of electromagnetic radiation is available. This radiation may be natural sunlight but inevitably must be artificial to accommodate seasonal, daily, and hourly changes due to winter, nightfall, and cloudiness.

Solid photocatalysis is a proven technology while dissolved photocatalysis is relatively new. With solid photocatalysis, reactions only occur if the species are adsorbed at the surface of the solid photocatalyst. The overall rate of the photocatalytic reactions are, thus, dependent on the concentration of the species, the rate of adsorption of the species, the available surface area of the photocatalyst, and the rate of desorption of the decomposition products. With dissolved photocatalysts, reactions occur in bulk solution and are only dependent on concentration. Consequently, reaction kinetics with dissolved photocatalysts can be at least three orders of magnitude faster than with solid photocatalysts.

## Results

All work for this project was completed. The final report was revised and published.

### ACTIVITY IV, PROJECT 3A: PHOTOASSISTED ELECTRON TRANSFER REACTIONS FOR METAL-COMPLEXED CYANIDE

#### Project Overview

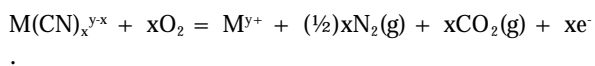
Previous research efforts under the Mine Waste Technology Program for the remediation of mine wastewaters predominantly focused on removing toxic heavy metal cations from solution. This was accomplished with chemical processes that generated heavy-metal sludges that were then removed from the water stream by solid-liquid separation processes. However, many of the anions associated with the heavy metal cations in the wastewater are also toxic but remain in solution even after the sludge is generated and separated. In this project, the remediation of metal-complexed cyanide is being investigated using several photolytic methods with the intent to identify and enhance naturally occurring remediation processes.

Overwhelming evidence shows that natural processes occur to heal environmental scars caused by mining activities. These processes include electron-transfer reactions that lower the concentrations of the anionic mobile toxic constituents in surface and groundwaters through interactions with electromagnetic radiation (predominantly UV radiation but some visible light) from the sun. However, such direct natural photolytic processes suffer at night, on cloudy days, and in winter months. During these periods, artificial radiation sources are needed for sustainment. Furthermore, because the photolytic processes usually proceed slowly, catalysts are used to absorb the radiation and transfer the energy to the reactants to remediate the water within more acceptable time frames. Such photocatalysts are

either solid semiconductors (heterogeneous photocatalysts) or dissolved radicals in solution (homogeneous photosensitizers).

#### Technology Description

**Background**—When electromagnetic radiation is absorbed, electrons in the absorbing species pass from a singlet ground state ( $S_0$ ) to an excited electronic state ( $S_1$ ). As long as the electron remains in the excited state, the absorbing species are more susceptible to their chemical environment and are, therefore, more apt to participate in electron-transfer reactions. The absorbing species undergo photoreduction when it donates the excited electron. Conversely, photooxidation occurs when the absorbing species accept an electron. In either case, the photoreduction and photooxidation reactions can lead to the destruction of the mobile toxic constituent. For metal-complexed cyanide, only photooxidation can be used and in a reaction similar to cyanide photooxidation (see Activity IV, Project 3) where carbon dioxide and nitrogen gases are reaction products:



**Direct Photolysis**—In this process, the mobile toxic constituent being remediated must absorb the electromagnetic radiation. Although this phenomenon is rare, it does occur with some metal-complexed cyanides but is dependent on the solution conditions. Research was conducted to identify these conditions.

**Homogeneous Photolysis**—In this process, aqueous photosensitizers absorb the electromagnetic radiation and then transfer the photon energy to the mobile toxic constituents being remediated. Because the process occurs in bulk solution, its kinetics are dependent on the solution conditions and the concentrations of the photosensitizers and the mobile toxic constituents. When the aqueous photosensitizer is not consumed during the process, it is referred to as homogeneous photocatalysis. In this regard, research is being conducted to identify the conditions needed for using either homogeneous



photosensitizers or homogeneous photocatalysts for metal-complexed cyanide remediation.

**Heterogeneous Photocatalysis**—In this process, solid semiconductors are used to absorb the electromagnetic radiation and then transfer the photon energy to the mobile toxic constituent being remediated. However, electron transfer reactions can only occur if the mobile toxic constituent is adsorbed at the surface of the semiconductor. Thus, reaction kinetics are dependent on the mobile toxic constituent concentration as well as the rate of adsorption of the constituent, the available surface area of the semiconductor, and the rate of desorption of the reaction products. Consequently, reaction kinetics can be three orders of magnitude slower than reactions with homogeneous photolysis.

Nevertheless, reaction efficiencies are usually higher with heterogeneous photocatalysis due to the higher efficiency of photon capture and the increased "life" of the electron in the excited state. This is ultimately attributed to the properties of the semiconductor. With semiconductors, electrons are promoted from the valence band and into the conductance band across a band gap. The photon energy must be greater than or equal to the band gap energy. Excited electrons in the conductance band can then be donated to the mobile toxic constituent to induce its reduction. Likewise, the electron vacancy or "hole" in the valence band can accept electrons from the mobile toxic constituent and thereby induce its oxidation. The process is similar to the process described earlier; however, it is evident that solution conditions must also be well-defined to control reactant adsorption and product desorption. In this regard, studies are being conducted to optimize these conditions for metal-complexed cyanide oxidation reactions. For now, only anatase (TiO<sub>2</sub>) is being investigated because it has the highest known efficiency of semiconductors.

## Results

This project was a continuation of the nitrate and cyanide project (Activity IV, Project 3) but with the inclusion of photolytic research on metal-

complexed cyanides. The final report was published.

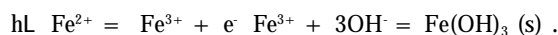
## ACTIVITY IV, PROJECT 3B: PHOTOASSISTED ELECTRON TRANSFER REACTIONS FOR BERKELEY PIT WATER

### Project Overview

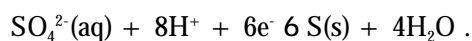
See Activity IV, Project 3A for Project Overview.

### Technology Description

**Background**—When electromagnetic radiation is absorbed, electrons in the absorbing species pass from a singlet ground state (S<sub>0</sub>) to an excited electronic state (S<sub>1</sub>). As long as the electron remains in the excited state, the absorbing species are more susceptible to their chemical environment and are, therefore, more apt to participate in electron-transfer reactions. The absorbing species undergo photoreduction when it donates the excited electron. Conversely, photooxidation occurs when the absorbing species accept an electron. In either case, the photoreduction and photooxidation reactions can lead to the precipitation of mobile toxic constituents. For example, ferrous cations can be precipitated as ferri-hydroxide after being photooxidized to ferric cations:

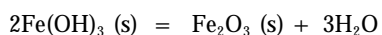


This reaction mechanism may account for the natural precipitation events observed in Berkeley Pit water. Once the iron is precipitated and separated, photolysis and/or conventional hydrometallurgical processes can then be used to recover the valuable mobile toxic constituents. On the other hand, a photoreduction reaction is exemplified by sulfate conversion to elemental sulfur:



Clearly, acid mine waters can be remediated through photolysis. However, it is important to note that several competing processes may occur and must be prevented and/or minimized to maximize the efficiency of photoassisted electron transfer reactions.

Nevertheless, reaction efficiencies are usually higher with heterogeneous photocatalysis due to the higher efficiency of photon capture and the increased "life" of the electron in the excited state. This is ultimately attributed to the properties of the semiconductor. With semiconductors, electrons are promoted from the valence band and into the conduction band across a band gap. The photon energy must be greater than or equal to the band gap energy. Excited electrons in the conduction band can then be donated to the mobile toxic constituent to induce its reduction. Likewise, the electron vacancy or "hole" in the valence band can accept electrons from the mobile toxic constituent and thereby induce its oxidation. The process is similar to the process described earlier; however, it is evident that solution conditions must be well-defined to control reactant adsorption and product desorption. In this regard, studies are being conducted to optimize these conditions for metal-complexed cyanide oxidation reactions. For now, both hematite ( $\text{Fe}_2\text{O}_3$ ) and anatase ( $\text{TiO}_2$ ) are being investigated. Hematite is important because it can actually be formed by recycling the precipitated ferrihydrite



whereas, the anatase is important because it has the highest known efficiency of semiconductors.

## Results

The final report was published.

## ACTIVITY IV, PROJECT 4: METAL ION REMOVAL FROM ACID MINE WASTEWATERS BY NEUTRAL CHELATING POLYMERS

### Project Overview

A bench-scale research project was conducted at Montana Tech of the University of Montana to eliminate or minimize some current economic or technical difficulties that exist in treatment technologies for acid mine wastewater. The novel technology was based on neutral chelating polymers that can have their chelating property turned on and off. The chelate switch was based on known electrochemical or photochemical properties of electrically conducting polymers.

### Technology Description

Chelates are chemical substances that have more than one binding site on the molecule; these added binding sites attach a molecule to a metal ion more strongly than a single binding site. The result is that chelates can be very effective at removing metal ions from wastewater. Chelates can be ionic or neutral. Ionic chelates exchange a cation ( $\text{H}^+$  or  $\text{Na}^+$ ) for the metal ion removed from the solution. Neutral chelates are electrically neutral and do not add material to the solutions when the metal ions are removed.

The removal of metal ions from aqueous solutions is presently accomplished by a variety of chemical and electrochemical processes. These techniques have distinct advantages in the appropriate situations (pH range, concentration range, matrix composition, etc.); however, they may not be practical under less-than-optimum operating conditions.

The goal of this project was to develop an alternate technology that required no additional chemicals, could produce a marketable product (such as pure metals), and could reduce costs and waste volume. The research project was a collaborative effort

between academic and government resources, including the Haskell Indian Nations Universities' Haskell Environmental Research Studies Center. Initially, the project focused on the design of chelating polymer systems for laboratory study and for theoretical study (molecular modeling). The first polymer systems were based on current literature information. Modeling results were compared to experimental and literature results as a means to test the validity of the theoretical data.

The validated modeling procedure was used to design and test a variety of neutral chelating systems for their capability to remove metal ions and associated anions from acid mine wastewater. The neutral chelating polymers determined to be most effective for water cleanup by the preliminary experimentation and the modeling studies were studied more thoroughly. The polymeric systems were evaluated for their removal efficiencies, contaminant capacity, ruggedness, ease of use, and cost effectiveness. Other important parameters identified in the preliminary studies were also used in the systems evaluations.

A more detailed process evaluation procedure was developed from the results of the refined experimentation. The selected polymeric system was then completely studied using a variety of synthetic and actual mine wastewater.

## Results

All work for this project was completed, and the final report was published.

## ACTIVITY IV, PROJECT 5: REMOVAL OF ARSENIC AS STORABLE STABLE PRECIPITATES

### Project Overview

The objective of this project was to strip arsenic from solutions in such a way as to produce apatite mineral-like precipitated products that are stable

for long-term storage in tailing pond environments. Substitution of arsenic into an apatite structure will provide a solid solution mineral compound that is environmentally stable for outdoor pond storage.

## Technology Description

Earlier research demonstrated that a precipitation technique is effective in removing arsenic (to low micrograms per liter concentrations) from aqueous solutions (EPA-supported project). The precipitation is conducted in a way to form a solid solution compound containing arsenate and phosphate in an apatite mineral-like phase. This solid is stable to EPA's toxicity characteristic leachate procedure, and more importantly, the solubility is one to two orders of magnitude less than calcium arsenate in aqueous solutions over the pH range of 9 to 12 (the range of pH values maintained in tailing ponds).

In the early 1980s, it was demonstrated that lime precipitation of calcium arsenate with subsequent storage in a tailings pond environment is unacceptable because at pH levels above approximately 8.5, calcium arsenate will be converted to calcium carbonate (by carbon dioxide in air) with the release of arsenic into the aqueous phase. Removal of arsenic by precipitation as calcium arsenate has been discontinued by industry and has been replaced by ferric arsenate precipitation (EPA's Best Demonstrated Available Technology for arsenic-bearing solutions). However, even though low concentrations of arsenic in solutions can be achieved by ferric precipitation, it has been demonstrated that the removal from solution is actually an adsorption phenomena. Therefore, long-term stability of such residues in tailings pond environments may not be appropriate, hence, the need for the present study.

Stability of Mineral-Like Residues—Montana Tech of the University of Montana researcher's approach to arsenic storage was to form a mineral-like phase that showed equilibrium-phase stability under tailings pond environmental conditions. If equilibrium-phase stability was achieved (for a given environment), then long-term stability

would be ensured (at least for as long as the environmental conditions were maintained). This project was supporting an intensive investigation of the formation of arsenic precipitates in two systems, i.e., the calcium-arsenic-phosphate (apatite-like solid solutions of arsenate and phosphate) system, and the ferric-arsenic-phosphate (phosphoscorodite-like solid solutions of arsenate and phosphate) system. Both of these systems showed great promise for industrial application, if long-term stability could be demonstrated.

## Results

The precipitation "recipe" was applied to two industrially contaminated waters, and the long-term stability of the resulting products were tested. Successful demonstrations resulted in a new way to treat arsenic-bearing wastewaters and mine drainage solutions.

All work for this project was completed, and the final report was published.

report from each test was forwarded for evaluation by the EPA Region VIII field office, and the EPA National Risk Management Research Laboratory.

## Results

Nine demonstrations were completed and reports are available.

## ACTIVITY IV, PROJECT 7: BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECT

### Project Overview

The purpose of the Berkeley Pit Innovative Technologies Project was to provide a test bed for high risk/innovative technologies for the remediation of Berkeley Pit water. The project focused on bench-scale testing of remediation technologies to help assist in defining alternative remediation strategies for EPA's future cleanup objectives for Berkeley Pit waters.

Individuals, companies, or academic institutions with existing remediation technologies were invited to demonstrate their process for the project and write a report summarizing their process including the results of their bench-scale test. A copy of the



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